

# SOVIET PHYSICS USPEKHI

*A Translation of Uspekhi Fizicheskikh Nauk*

SOVIET PHYSICS USPEKHI

Russian Vol 74, Nos. 3-4

JANUARY-FEBRUARY 1962

## THE STUDY OF NONEQUILIBRIUM PHENOMENA IN SHOCK WAVES

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Usp. Fiz. Nauk 74, 393-434 (July, 1961)

### CONTENTS

1. Introduction . . . . .	525
2. Qualitative picture of the processes occurring in a shock wave . . . . .	526
3. Theoretical examination of the individual processes leading to the establishing of equilibrium . . . . .	527
3.1. Establishing of the Maxwell distribution . . . . .	527
3.2. Establishing of equilibrium in the vibrational degrees of freedom (vibrational relaxation) . . . . .	528
3.3. Establishing of equilibrium in the rotational degrees of freedom (rotational relaxation) . . . . .	531
3.4. Establishing of the equilibrium degree of dissociation . . . . .	531
3.5. Establishing of the equilibrium degree of ionization . . . . .	533
4. Functioning of a shock tube . . . . .	534
5. Experimental methods for studying the state of a gas in a shock wave . . . . .	537
5.1. Measurement of the density of the gas . . . . .	537
5.2. Measurement of the concentrations of the components of the gas . . . . .	538
5.3. Measurement of the intensity of radiation . . . . .	539
5.4. Measurement of the temperature of the gas . . . . .	541
5.5. Measurement of the concentration of electrons . . . . .	543
5.6. Measurement of the pressure . . . . .	544
5.7. Measurement of the speed of flow . . . . .	544
6. Summary of results . . . . .	545
6.1. The establishing of the Maxwell distribution (monatomic gas) . . . . .	545
6.2. Rotational relaxation . . . . .	545
6.3. Vibrational relaxation . . . . .	546
6.4. Dissociation of diatomic molecules . . . . .	547
6.5. Ionization . . . . .	548
Literature cited . . . . .	548

### 1. INTRODUCTION

THE propagation of a strong shock wave in a gas is accompanied by a sharp change of its state, leading to a destruction of the statistical equilibrium in the medium. The study of the process of establishing equilibrium in shock waves has made it possible to obtain valuable information about the kinetics of relaxation processes in gases, which are of interest both for the aerodynamics of large supersonic velocities and also in certain problems of physical kinetics and the kinetics of chemical reactions in gases at high temperatures. These phenomena include the establishing of

the Maxwell distribution in the translational degrees of freedom of the molecules, the excitation of molecular rotation and vibrations, the thermal dissociation of molecules, emission of radiation, and ionization.

The present paper is devoted to a survey of the main methods and results of theoretical and experimental studies of the various relaxation phenomena in shock waves. In the first part of the paper (Secs. 2 and 3) we give a theoretical treatment of the processes of establishing equilibrium in the separate degrees of freedom; this treatment is based on the kinetic theory of gases. The phenomenological method of description of states of incomplete statistical equi-

librium, based on the introduction of supplementary parameters,<sup>35</sup> is not considered in this paper. The second part of the paper (Secs. 4 and 5) is devoted to the experimental study of the states of gases in shock waves. At the present time these studies are made with various kinds of apparatus—shock tubes,<sup>81,157</sup> explosion chambers,<sup>94</sup> pulse apparatus,<sup>34</sup> and so on. Here we shall consider the methods of investigation that are used in work with shock tubes—the simplest laboratory apparatus, and that which yields the greatest number of results on the kinetics of relaxation processes at high temperatures. In this paper we consider only endothermic processes in gases; some features of the occurrence of exothermic processes in shock waves (detonations) have been discussed in a paper published in this journal by R. I. Soloukhin,<sup>56</sup> and also in other review articles,<sup>52,118</sup> and have been studied in more detail by Zel'dovich and Kompaneets.<sup>15</sup>

The questions with which we deal have been subject to development only in recent years; one of the first papers in this field is by Ya. B. Zel'dovich, who studied the broadening of shock waves on account of the retarded excitation of vibrations.<sup>16</sup> The present paper is a sequel to the well known article by Ya. B. Zel'dovich and Yu. P. Raizer,<sup>17</sup> and is devoted to the consideration of the nonequilibrium phenomena that accompany the propagation of shock waves in gases.

## 2. QUALITATIVE PICTURE OF THE PROCESSES OCCURRING IN A SHOCK WAVE

A shock wave is a layer of definite thickness separating two equilibrium states of a gas. By an equilibrium state we mean a state of complete statistical equilibrium, which means equilibrium among all degrees of freedom, including equilibrium between atoms, molecules, electrons, and ions. Under some conditions a state of complete statistical equilibrium in a shock tube is not attained even at the surface of contact. In this connection it is helpful to introduce the concept of the front of the shock wave, by which we mean the zone in which the Maxwellian equilibrium is established. In this case we can speak of the nonequilibrium processes occurring behind the front of a shock wave. We are justified in distinguishing the front of a shock wave by the fact that for processes behind the front we can introduce the concept of temperature. The passage of the gas from one equilibrium state to another which is caused by the shock wave is a complex process, consisting of separate and often overlapping processes of establishing of equilibrium in the different degrees of freedom. Owing to this it will be helpful to preface the survey of the experimental study of these processes with a theoretical examination of the general picture of the excitation of the various degrees of freedom. When we have a preliminary set of relaxation times corresponding to the various degrees of freedom, we can try to separate the

individual stages in the general process of the establishing of equilibrium and to study each in isolation. At temperatures not higher than 10,000°K the main processes that lead to the establishing of thermodynamic equilibrium are processes of the transfer and transformation of energy in molecular collisions. The sequence of the excitations of the various degrees of freedom of emission of light can be neglected. The sequence of the excitations of the various degrees of freedom of the molecules is determined by the numbers of collisions needed for the excitation of the various degrees of freedom. The number of collisions needed for the excitation of any particular degree of freedom of a molecule depends on the probability of the transfer or transformation of the energy in a collision. The calculation of the probabilities for the transformations of energy is made by quantum-mechanical methods, and in doing so one can treat the relative translational motion of the colliding molecules classically.<sup>50</sup> This justifies the use of classical concepts of the number of collisions and the time of free motion along with the quantum-mechanical probabilities.

As is well known, the most rapid process is that of energy transfer between translational degrees of freedom, which occurs in a time of the order of the mean time between collisions. This process leads to the establishing of the Maxwell distribution. As we shall see hereafter, all of the other degrees of freedom are excited much more slowly. This gives us the right to average our probabilities for the transformations in inelastic collisions by using the Maxwell distribution, i.e., to use the idea of a temperature of the translational degrees of freedom.

The excitation of the internal degrees of freedom of the molecules is a much more complicated process. We can get a qualitative understanding of the character of the process of excitation of the internal degrees of freedom if we use the following model: we regard the molecule as a classical oscillator, and treat the collision process as the action of an external force on the oscillator. In this case it is well known<sup>23</sup> that the effectiveness of an inelastic collision, i.e., the amount of energy transferred in the collision, is determined by the value of  $\omega\tau$ , where  $\omega$  is the frequency of the oscillator and  $\tau$  is the duration of the collision. In the case  $\omega\tau \gg 1$ , which corresponds to almost adiabatic collisions, the amount of energy transferred in a collision is small; in the opposite case  $\omega\tau \ll 1$ , corresponding to strongly nonadiabatic collisions, excitation of internal degrees of freedom can occur relatively easily. These results remain valid also in quantum theory, except that in this case we must use  $\Delta E/\hbar$  instead of  $\omega$ . In the case of vibrational degrees of freedom  $\omega\tau \gg 1$ , and therefore some tens of thousands of collisions are required for the excitation of the molecular vibrations. (This number can vary considerably, depending on the temperature and other conditions.) For rotational degrees of freedom  $\omega\tau \ll 1$  (the light

gases are the only exceptions), and therefore the excitation of rotation occurs relatively easily, in a time of the order of ten collisions.

The first quantitative calculation of the probability of excitation of vibrational degrees of freedom, based on these ideas, was made by L. D. Landau and E. Teller.<sup>25</sup> As has been proved recently,<sup>42</sup> their values of the probabilities agree exactly with the results of a consistent quantum-mechanical calculation.<sup>169,170</sup> The probability of excitation of the vibrational energy is of the form

$$P \sim \exp(-2\pi\omega\tau),$$

where  $\omega = \Delta E/\hbar$ ,  $\tau = a/v$ , and  $a$  is the mean radius of the intermolecular interaction. After averaging over the Maxwell velocity distribution this formula takes the form

$$P \sim \exp(-3\chi), \quad \chi = \left( -\frac{\pi^2 a^2 (\Delta E)^2 \mu}{\hbar^2 \cdot 2kT} \right)^{1/3}. \quad (2.1)$$

For various gases at room temperature  $\chi$  varies<sup>170</sup> over the range from 5 to 10. The expression (2.1) is known in the literature as the Landau-Teller formula.

The slowest processes of establishing equilibrium are those associated with dissociation and ionization.\* This is explained by the fact that dissociation and ionization of molecules can occur only in cases in which the colliding molecules have a sufficient supply of energy. Since such molecules are in the tail of the Maxwell or Boltzmann distribution, there are only a few of them, and consequently the process of the establishing of the equilibrium dissociation and ionization will go very slowly. The upper limit for its rate, i.e., for the probability of such processes, will be determined by the equilibrium number of molecules possessing the necessary energy  $E$ ; that is, the probability of dissociation in a collision satisfies the relation

$$P_D \sim \exp\left(-\frac{E}{kT}\right).$$

Since under ordinary conditions  $E/kT \gg 1$ , we have  $P_D \ll P$ . This means that the process of establishing the equilibrium dissociation and ionization will occur more slowly than that of establishing equilibrium in the vibrational degrees of freedom.

Thus the sequence of processes of excitation of the various degrees of freedom, i.e., the sequence in which equilibrium is established in the various degrees of freedom, is as follows. First, after a time of the order  $\tau_1$ , excitation of the translational degrees of freedom will have occurred and the Maxwell distribution will be established. Then, after a time  $\tau_2$ , rotational equilibrium will be established, and after a time  $\tau_3$ , vibrational equilibrium.

The slowest processes are those of establishing the equilibrium degree of dissociation (relaxation time  $\tau'_4$ ) and of ionization (relaxation time  $\tau''_4$ ).

\*It is assumed that  $kT \ll D$ , where  $D$  is the dissociation energy.

Thus under actual conditions for pure gases the following inequality can be satisfied:\*

$$\tau_1 \ll \tau_2 \ll \tau_3 \ll \tau'_4, \tau''_4.$$

This relation decidedly simplifies the experimental study of the processes and facilitates the theoretical treatment of the problem, since each of the various processes can be considered in isolation, with the assumption that the preceding process has been completed and that the next one has not yet started.<sup>33</sup> We emphasize that this sort of distribution of the values of the relaxation times for the various processes is characteristic only of pure gases at not too high temperatures. In mixtures this sequence of relaxation times may not hold. For example, in air<sup>28</sup> the vibrational relaxation time for  $N_2$  is of the same order as the time for establishing the equilibrium degree of dissociation for  $O_2$ .

### 3. THEORETICAL EXAMINATION OF THE INDIVIDUAL PROCESSES LEADING TO THE ESTABLISHING OF EQUILIBRIUM

3.1. Establishing of the Maxwell Distribution. The first attempts at a theoretical determination of the thicknesses of the fronts of shock waves in monatomic gases were of a hydrodynamic nature. The thickness of the front of a shock wave was calculated by means of the equations of a viscous and thermally conducting medium. The outline of the solution and the results are presented in detail in references 19 and 24. It follows from this solution that for strong shock waves the thickness of the front is of the order of the mean free path. This result shows mainly that the thickness of the front of a strong shock wave cannot be determined by hydrodynamical methods. As is well known, the equations of hydrodynamics are valid when the changes of macroscopic quantities over a distance of a mean free path are small, but this condition is not satisfied in the case of strong shock waves. The derivation of the hydrodynamic equation in the kinetic theory of gases is based on the solution of Boltzmann's kinetic equation by the Enskog-Chapman method; therefore to determine the thickness of the front of a strong shock wave it is necessary to start directly from the Boltzmann equation. The usual methods for solving the Boltzmann equation are based on perturbation theory, with the Maxwell distribution function taken as the zeroth approximation. The Enskog-Chapman method is of this sort, and the method of moments is also usually applied in this sort of approximation. These methods are not valid for the description of the structure of the front of a strong shock wave, since the shock wave leads to a violent disturbance of the state of the gas. To describe the structure of the front in a strong shock wave one needs a method which would take into account the finiteness of the

\*Concerning the condition  $\tau_2 \gg \tau_1$  cf. Sec. 6.2.

perturbations in the very first approximation. Such a method for the solution of the Boltzmann equation has been proposed by Mott-Smith.<sup>146</sup> His arguments are as follows. Since the thickness of the front of the shock wave is of the order of the mean free path, we can expect that the front of the shock wave is partially penetrated by considerable numbers of molecules from the supersonic and subsonic streams, which obey the Maxwell distribution. This suggests that a characteristic feature of the velocity distribution in the front of a strong shock wave is that there are two maxima, determined by the temperatures of the supersonic and subsonic streams. On the basis of these arguments, Mott-Smith proposed taking as the first approximation to the solution of the Boltzmann equation a sum of two Maxwellian functions, which in the one-dimensional case is of the form

$$f^{(0)} = \nu_\alpha(x) f_\alpha + \nu_\beta(x) f_\beta, \quad (3.1)$$

where  $f_\alpha$  and  $f_\beta$  are Maxwellian functions corresponding to the supersonic and subsonic flows, and  $\nu_\alpha(x)$  and  $\nu_\beta(x)$  are the densities of the supersonic and subsonic components, referred to the densities of the unperturbed gas in the supersonic and subsonic regions, respectively. As can easily be seen, the expression (3.1) is not a solution of the Boltzmann equation, and therefore to determine the unknown functions  $\nu_\alpha(x)$  and  $\nu_\beta(x)$  Mott-Smith used the transport equation. It follows from the solution of the transport equation that

$$\nu_\alpha(x) = \nu(-x), \quad \nu_\beta(x) = \nu(x), \quad \nu(x) \equiv \frac{1}{2} \left( 1 + \tanh \frac{2x}{X} \right). \quad (3.2)^*$$

The origin of coordinates is at the center of the front of the shock wave. The form of the function  $X$  is determined by the choice of the transport function. Later, in references 165 and 166, it was shown that a function  $X$  can be found such that for large numbers  $M$  the expression is a solution of the Boltzmann equation in a finite domain in velocity space. As can be seen from Eq. (3.2), the width of the shock is determined by the value of  $X$ . For the rigid-sphere model the calculated values of  $X$  are (for various values of the number  $M$ )

$M$	$\infty$	10	5	4	3	2.5
$l/X$	0.703	0.685	0.630	0.596	0.520	0.474,

where  $l = (2^{1/2} \pi n_a \sigma^2)^{-1}$  is the mean free path in the unperturbed supersonic flow.

Thus for large  $M$  the shock front thickness is about twice the mean free path in the unperturbed gas. Experimental studies of the shock thickness are in good agreement with the theory of Muckenfuss (see reference 119), which is based on the use of a bimodal distribution (see Sec. 6.1). A direct comparison of the experimental data<sup>119</sup> with the results of Mott-Smith is difficult; the latter results are good only for large numbers  $M$ .

\*th = tanh.

The process of establishing the Maxwell distribution in a gas mixture is rather complex. In particular, in a binary mixture of a heavy gas and a small amount of a light gas the process of establishing the Maxwell distribution will occur in two stages. First, during a time of the order of the mean time between collisions, the Maxwell distribution is established in the heavy gas. Then there begins the process of establishing the Maxwell distribution in the light gas, and the relaxation time of this process is  $M/m$  times that of the first process ( $M$  is the mass of the heavy gas).<sup>46</sup> In the case when the concentration of the light gas is not low, the fast process will lead to each of the gases having its own Maxwell distribution. The slow process will consist of equalization of the temperatures of the two distributions, that is, the establishing of a single Maxwell distribution.

**3.2. Establishing of Equilibrium in the Vibrational Degrees of Freedom (Vibrational Relaxation).** The theory of vibrational relaxation has been much more completely developed than the theory of rotational relaxation. Since the latter theory is largely constructed on the model of the former, we shall first consider the theory of vibrational relaxation.

Let us begin with the study of the simplest case—the vibrational relaxation of a small amount of diatomic gas mixed with a large amount of monatomic gas. This case is especially convenient for theoretical and experimental treatment, since the vibrational relaxation in such a mixture does not lead to any appreciable change of the temperature of the translational degrees of freedom and the main process leading to the relaxation is the conversion of kinetic energy of the atoms into vibrational energy of the molecules. In this case we can neglect the collisions of the molecules with each other. The system of equations that describes the vibrational relaxation is the system of equations of balance for the numbers of molecules in the various vibrational levels. If we denote by  $x_n(t)$  the concentration of molecules in the  $n$ -th vibrational level, this system takes the form

$$\frac{dx_n}{dt} = Z \left( \sum_{m \neq n} P_{mn} x_m - x_n \sum_{m \neq n} P_{nm} \right) \quad (3.3)$$

where  $Z$  is the number of collisions per second experienced by a molecule and  $P_{ij}$  is the probability for transition of a molecule from the  $i$ -th to the  $j$ -th state in a collision with an atom. The probability  $P_{ij}$  is given by the formula (2.1). Because of the exponential dependence of  $P_{ij}$  on the energy  $\Delta E_{ij}$  the only transitions that are permitted in practice are those to neighboring levels. This statement is true up to temperatures of the order of the characteristic temperatures.

Thus the system (3.3) can be written in the form

$$\frac{dx_n}{dt} = Z \{ P_{n+1, n} x_{n+1} - [P_{n, n-1} + P_{n, n+1}] x_n + P_{n-1, n} x_{n-1} \}, \quad n = 0, 1, 2, \dots \quad (3.4)$$

The concrete form of  $P_{mn}$  depends on the molecular model chosen.\* The simplest model that gives a sufficiently accurate description of the behavior of the molecules in the lower vibrational levels is the harmonic-oscillator model. For the oscillator<sup>25</sup>

$$P_{n+1, n} = (n+1)P_{10}, \quad (3.5)$$

and the system (3.4) takes the form

$$\frac{dx_n}{dt} = ZP_{10} \{ (n+1)x_{n+1} - [(n+1)e^{-\theta} + n]x_n + ne^{-\theta}x_{n-1} \},$$

$$P_{01} = P_{10} e^{-\theta}, \quad \theta = \frac{h\omega}{kT}, \quad n = 0, 1, 2, \dots \quad (3.6)$$

The initial conditions for (3.6) are given in the form  $x_n(0) = f_n(0)$ . We emphasize that the system (3.6) will describe satisfactorily only those characteristics of the actual relaxation process that are associated with the lower vibrational levels. The solution of the system (3.6) completely determines the process of vibrational relaxation of harmonic oscillators. In a macroscopic study of the relaxation process one is interested not in the changes of the numbers of molecules in individual levels, but in the changes of certain macroscopic characteristic quantities, in particular the vibrational energy.

We can obtain the relaxation equation for the vibrational energy from the system (3.6) without solving this system. Let us multiply Eq. (3.6) by  $h\omega n$  and sum over  $n$ . After some simple manipulation we get the following equation:

$$\frac{dE}{dt} = -ZP_{10}(1 - e^{-\theta}) \left\{ E - \frac{e^{-\theta}h\omega}{1 - e^{-\theta}} \right\}, \quad (3.7)$$

where  $E = h\omega \sum n x_n(t)$ . The last term in the curly brackets is the equilibrium value  $E_{eq}$  of the vibrational energy. One can readily verify this by writing it in the form

$$h\omega \frac{e^{-\theta}}{1 - e^{-\theta}} \equiv h\omega (1 - e^{-\theta}) \sum n e^{-n\theta}.$$

Thus the relaxation equation for the vibrational energy is

$$\frac{dE}{dt} = -\frac{1}{\tau} (E - E_{eq}), \quad (3.8)$$

where

$$\tau = \frac{1}{ZP_{10}(1 - e^{-\theta})}.$$

This is the general form of the relaxation equation for any macroscopic parameter which characterizes the lack of equilibrium at small deviations from equilibrium. For the oscillator itself this equation is valid for arbitrary deviations from equilibrium. Replacement of the system (3.6) by the equation (3.8) means that the picture of the changes of the numbers of molecules in the vibrational levels is left obscure. In fact, the solution of Eq. (3.8),

\*The model determines the proportionality constant in Eq. (2.1), which depends on the square of the matrix element of an intramolecular coordinate.

$$E(t) - E_{eq} = (E(0) - E_{eq}) \exp\left(-\frac{t}{\tau}\right) \quad (3.9)$$

depends only on the total vibrational energies at the initial and final times and does not depend on the way the molecules are distributed over the vibrational levels for a given value of the total vibrational energy. It is seen from Eqs. (3.8) and (3.9) that the relaxation time of the total energy is

$$\tau = \frac{1}{ZP_{10}(1 - e^{-\theta})}. \quad (3.10)$$

This quantity is experimentally measurable. A comparison of the theoretical and experimental values of  $P_{10}$  for various gases at temperatures 300–600°K has been made in reference 170 and is discussed in Sec. 6.3.

Except in a few cases, the agreement is very good. In recent years studies have been made on vibrational relaxation in shock tubes at higher temperatures (Sec. 5). In particular, in reference 77 the vibrational relaxation of  $O_2$  has been studied up to the temperature 3000°K. The values of  $P_{10}$  found in this way agree with the values of Schwartz and Herzfeld, which were calculated earlier and subsequently corrected.<sup>170, 123</sup>

Temperature, °K	$P_{10exp}$	$P_{10theor}$
288	$4 \cdot 10^{-8}$	$4 \cdot 10^{-8}$
900	$1.1 \cdot 10^{-5}$	$1.2 \cdot 10^{-5}$
1200	$2.4 \cdot 10^{-5}$	$5.2 \cdot 10^{-5}$
1800	$9.8 \cdot 10^{-5}$	$3.4 \cdot 10^{-4}$
2400	$3.7 \cdot 10^{-4}$	$2.2 \cdot 10^{-3}$
3000	$1.2 \cdot 10^{-3}$	$6 \cdot 10^{-3}$

We emphasize that as the temperature is changed from 300°K to 3000°K the value of  $P_{10}$  changes by five orders of magnitude, with agreement between the experimental and theoretical data over the entire temperature range. This is a good confirmation of the theory of vibrational relaxation which has been presented.

For an analysis of the microscopic picture of the process of establishing equilibrium it is necessary to start with the general solution of Eq. (3.6).

Before we develop the methods for finding the general solution, let us consider a particular solution which is of great practical importance. Suppose that at the initial time the distribution of the oscillators over the vibrational levels is a Boltzmann function with a temperature different from the temperature of the translational degrees of freedom of the gas. This sort of initial condition is typical of the gas behind the front of a shock wave, if by the front we mean the zone in which the establishing of the Maxwell distribution occurs. Immediately behind the front of the shock wave the translational temperature has already taken a new value, but the vibrational temperature still has its old value, equal to the translational temperature of the unperturbed gas in front of the shock wave.

Thus

$$x_n(0) = (1 - e^{-\theta_0}) e^{-n\theta_0}.$$

We look for a solution of the system of equations (3.6) in the form

$$x_n(t) = (1 - e^{-\vartheta(t)}) e^{-n\vartheta(t)}, \quad (3.11)$$

where

$$\vartheta(0) = \vartheta_0.$$

Substituting Eq. (3.11) in Eq. (3.6), we get only one equation

$$\frac{d\vartheta}{dt} = ZP_{10}(1 - e^{-\vartheta}) [e^{-\vartheta} - e^{-\vartheta_0}] e^{\vartheta}. \quad (3.12)$$

The solution of Eq. (3.12) is

$$\vartheta(t) = \ln \left[ \frac{e^{-\frac{t}{\tau}(1 - e^{\vartheta_0 - \vartheta_0})} - e^{\vartheta_0}(1 - e^{-\vartheta_0})}{e^{-\frac{t}{\tau}(1 - e^{\vartheta_0 - \vartheta_0})} - (1 - e^{-\vartheta_0})} \right]$$

Thus in the special case of the initial conditions (3.10) the process of establishing equilibrium in the vibrational degrees of freedom occurs in such a way that the distribution function keeps its original form and only the temperature changes. We emphasize that this assertion is valid only for the model of the harmonic oscillator. An analogous case is also encountered in the establishing of the Maxwell distribution.<sup>46</sup> We note that in the case of the initial Boltzmann distribution the process of establishing the equilibrium populations goes on simultaneously in all of the levels. For other initial conditions this synchronism can be destroyed. In particular, if the initial distribution is of the  $\delta$  type, corresponding to one of the first levels, the process of populating the upper levels will be delayed relative to that of populating the lower levels.

The general solution of (7) is of the form

$$x_n(t) = \sum_{\mu_i} A_{\mu_i} l_n(\mu_i) e^{\mu_i t},$$

where  $\mu_i$  and  $l_n(\mu_i)$  are the eigenvalues and eigenfunctions of the matrix of the coefficients of the system (3.6). It is shown in reference 145 that  $\mu_i = -ZP_{10}(1 - e^{-\vartheta}) i$  and  $l_n(\mu_i)$  are Gottlieb polynomials.

It is more convenient, however, to solve (3.6) by the generating-function method. We introduce the function  $G(z, t) = \sum z^n x_n(t)$ . Multiplying (3.6) by  $z^n$  and summing over all  $n$ , after simple manipulations we get the equation for the generating function,

$$\frac{1}{k} \frac{\partial G}{\partial z} = (z - 1) e^{-\vartheta} \left\{ \frac{\partial G}{\partial z} [(z - 1) + (1 - e^{\vartheta}) + G] \right\}, \quad k = ZP_{10}.$$

The solution of (3.13) is of the form

$$G(z, t) = \frac{1 - e^{\vartheta}}{(z - e^{\vartheta}) - (z - 1) e^{-\frac{t}{\tau}}} G_0 \left( \frac{(z - 1) e^{-\frac{t}{\tau}} e^{\vartheta} - (z - e^{\vartheta})}{(z - 1) e^{-\frac{t}{\tau}} - (z - e^{\vartheta})} \right), \quad (3.14)$$

where the function  $G_0(y)$  is determined by the initial conditions

$$G_0(y) \equiv G(y, 0) = \sum y^n x_n(0).$$

A detailed treatment of the solutions that correspond to various initial conditions is given in reference 145.

Up to now our treatment has been confined to systems in which diatomic gases are present only as small amounts of impurities. The question arises as to how vibrational relaxation will occur in a system composed entirely of diatomic molecules. In a system with a small amount of a diatomic gas the main process in the relaxation is the conversion of energy of translational motion of the surrounding gas into vibrational energy of the molecules. In relaxation in a system entirely composed of diatomic molecules, besides the process just indicated there is also a process of transfer of vibrational energy in collisions between two molecules. Moreover, in the relaxation process in such a system the temperature of the translational degrees of freedom does not stay constant, but decreases. References 48 and 173 are devoted to the study of the part played by the process of transfer of vibrational energy in establishing equilibrium. The effect of the changes of temperature has been studied in reference 121. It is shown in reference 48 that in an isolated system of diatomic molecules the process of establishing equilibrium in the translational degrees of freedom occurs in two stages. As the result of the first, rapid stage the available vibrational quanta are redistributed among the molecules in such a way as to establish a quasi-stationary Boltzmann distribution with the temperature determined by the original supply of vibrational quanta and independent of the other initial conditions.

In the second, slow stage of the process there begins the conversion of translational energy into vibrational energy, which results in the evolution of the quasi-stationary distribution into the equilibrium distribution; in this stage the distribution maintains the Boltzmann form and only its temperature changes. The entire treatment has been carried out for the harmonic-oscillator model. Under usual experimental conditions the gas before the front of a shock wave is in an equilibrium state. Consequently the initial condition for the vibrational equilibrium is a state of the gas for which one can speak of two temperatures corresponding to the translational and vibrational motions. Since, according to the foregoing discussion, the relaxation process occurs in such a way that the temperature of the vibrational motion always has a meaning (the form of the Boltzmann distribution is maintained), in this case processes involving transfer of vibrational quanta are of no importance. Thus one can discuss the relaxation of the vibrational motion in an isolated system of molecules without taking into account processes of transfer of vibration.

As is shown in reference 121, the decrease of the translational temperature in the process of vibrational relaxation leads to an increase of the relaxation time. This is due to the fact that  $P_{10}$ , which determines the relaxation time (3.8), becomes a decreasing function

of the time. In this case Eq. (3.9) is not the solution of Eq. (3.8).

Up to now our discussion has been confined to pure diatomic gases and mixtures of diatomic and monatomic gases. The case of a mixture of diatomic gases is also of practical interest. As is well known, air is such a mixture. The vibrational relaxation time of a gas mixture is an over-all characteristic of the mixture. In particular, if both gases, A and B, possess vibrational degrees of freedom and there is no transfer of vibrational quanta between them, the relaxation time  $\tau$  of the whole mixture is practically determined by the larger of the relaxation times of the vibrational motions of the two components taken separately. An exchange of vibrational quanta can change the value of  $\tau$ . Since the characteristic time associated with the exchange of vibrations is usually shorter than the larger of the relaxation times for the vibrational motions of the individual components, the value of  $\tau$  will be determined either by the smaller of the relaxation times for the vibrational motions of the separate components or by the characteristic time associated with the transfer of vibrations.<sup>47</sup>

**3.3. Establishing of Equilibrium in the Rotational Degrees of Freedom (Rotational Relaxation).** The theory of rotational relaxation of the molecules is constructed in analogy with the theory of vibrational relaxation, but not much success has been achieved in this way.

Since the rotational relaxation time of the molecules is larger (or much larger) than the time for establishing the Maxwell distribution and much smaller than the vibrational relaxation time, there is justification for taking as the model of the rotating molecule the rigid-rotator model and assuming that the speeds of translational motion of the centers of mass of the molecules obey the Maxwell distribution. The simplest case of rotational relaxation is that of a system consisting of a monatomic gas with a small admixture of rotators. To get qualitative results one naturally assumes, in analogy with the case of the harmonic oscillator, that in the collision of a rotator with an atom the only allowed transitions are those between adjacent levels. This assumption is justified for light molecules<sup>85,176,177</sup> and is not valid for heavy ones. In this case the relaxation equations are analogous to those for vibrational relaxation, Eq. (3.6). A detailed derivation of these equations and a discussion of methods for their solution are given in reference 120. The results obtained in that paper are not encouraging. The theoretical value of the rotational relaxation time obtained for  $N_2$  and  $O_2$  is about two orders of magnitude larger than the experimental value. The cause of this large discrepancy lies in the fact that the establishing of rotational equilibrium occurs not by way of successive transitions between adjacent levels, but more rapidly. This effect finds its natural explanation

in the nonadiabatic character of the collisions that are accompanied by rotational transitions.

The next step is the construction of a theory that would take into account the possibility of many-quantum transitions in the rotational excitation. For many-step transitions the quantization of the rotations becomes unimportant and the problem can be formulated in terms of classical mechanics. One of the possible formulations of the problem is as follows. First one determines from a classical treatment of the collision of a rotator with some other particle the amount of increase of the rotational energy, which is then averaged over the Maxwell velocity distribution and over all possible orientations of the colliding particles. The ratio of the average amount of rotational energy per rotator in the equilibrium state to the increase so found can serve as a characteristic time for the establishing of rotational equilibrium. Such a program has been carried out in reference 149. If we define the number of collisions required to establish rotational equilibrium in the gas ( $Z_{rot}$ ) as the ratio of the time of rotational relaxation to the mean free time, we get from reference 149 the following expression for  $Z_{rot}$ :

$$Z_{rot} = \frac{Z_{rot}^{\infty}}{1 + \frac{\pi^2}{2} \left( \frac{T^*}{T} \right)^{\frac{1}{2}} + \left( \frac{\pi^2}{4} + \pi \right) \left( \frac{T^*}{T} \right)}, \quad (3.15)$$

where  $Z_{rot}^{\infty} = 1/16 (\alpha d/\epsilon)^2$ ,  $\alpha^{-1}$  is the effective radius of action of the intermolecular forces,  $d$  is the inter-nuclear distance in the molecule, and  $\epsilon$  is a parameter characterizing the asymmetry of the intermolecular interaction that is responsible for the excitation of rotational states. This result may make it possible to understand certain anomalies in the variation of the thickness of the front of a shock wave with the temperature.<sup>149</sup>

A theoretical calculation of  $Z_{rot}$  for  $Cl_2$ ,  $N_2$ , and  $O_2$  has been made in reference 149. This paper also gives an analysis of the available experimental data. The final results are in satisfactory agreement with the experimental and theoretical data (see Sec. 6.2). It must be remembered, however, that the theoretical approach that has been explained is a qualitative one and does not answer the question of the behavior of the distribution of the rotators over the rotational levels and of the roles of various collisions in the process of establishing the rotational equilibrium. A somewhat more quantitative approach to the study of this problem has been indicated in reference 189.

**3.4. Establishing of the Equilibrium Degree of Dissociation.** In studying the process of establishing the equilibrium degree of dissociation it is necessary first of all to understand the mechanism of the thermal dissociation of diatomic molecules. As is well known, the thermal dissociation of diatomic molecules occurs as the result of binary collisions of molecules. The number of collisions that lead to dissociation is only a small fraction of the total number of collisions. Two

main questions arise in this connection: first, what conditions the colliding molecules must satisfy in order for dissociation to occur, and second, how often these conditions are realized in the system in which the reaction is going on. The so-called elementary theory of collisions<sup>63</sup> solves these questions in the following way: it is assumed that there is a probability  $\alpha$  for dissociation of those colliding molecules whose energy (the energy of the internal degrees of freedom plus the kinetic energy of the relative motion along the line of centers) is not smaller than the dissociation energy. The dissociation probability  $\alpha$  is assumed not to depend on the other characteristics of the initial state of the colliding molecules and is subsequently determined from experiment. The second question—how often the conditions necessary for dissociation are encountered—is answered by the elementary theory of collisions on the assumption that the process of dissociation does not disturb the equilibrium distribution of the molecules over the energy levels.

The results obtained in this way are not in contradiction with the experimental data, but from the theoretical point of view the solution of the problem is not a consistent one, since there is a certain arbitrariness in both of the main points of the theory. The probability  $\alpha$  that appears in the theory of collisions should essentially be calculated as a function of the initial state of the colliding molecules. These probabilities in turn should determine the distribution of the molecules over the energy levels as the solution of the gas-kinetic equations. Furthermore one cannot say in advance under what conditions and to what extent this distribution will be an equilibrium distribution. In this connection the problem arises of a rigorous formulation of the gas-kinetic equations which describe the process of dissociation. In accordance with references 20 and 22, we assume that the main, though not the only, mechanism of dissociation is the transition of molecules from discrete vibrational states to continuous states. The probabilities of such transitions have been studied in reference 45, where it is shown that dissociation can occur only as the result of transitions of molecules from highly excited vibrational levels to the continuous spectrum. Transitions from lower levels are practically forbidden. This result can also be obtained qualitatively from the Landau-Teller formula (2.1). Because of the exponential dependence of the probability  $P$  on  $\Delta E$  the probability  $P$  will be different from zero practically only for transitions from highly excited levels.

These arguments enable us to write down uniquely the system of gas-kinetic equations that describes the process of dissociation. This system of equations will be analogous to the system that describes the vibrational relaxation, the only difference being that in the upper levels there will be the effect of a negative source, which describes the process of breakup of molecules into atoms.

Just as in the case of the vibrational relaxation, we at first suppose that the dissociating gas is present as a small admixture in a monatomic gas.

In this case the kinetic equations are of the form

$$\left. \begin{aligned} \frac{dx_n}{dt} &= Z \{ P_{n+1, n} x_{n+1} - [P_{n, n-1} + P_{n, n+1}] x_n + P_{n-1, n} x_{n-1} \}, \\ & n = 0, 1, \dots, k-1, \\ \frac{dx_k}{dt} &= Z \{ P_{d, k} x_d^2 - [P_{k, d} + P_{k, k-1}] x_k + P_{k-1, k} x_{k-1} \}, \\ \frac{1}{2} \frac{dx_d}{dt} &= Z \{ P_{k, d} x_k - P_{d, k} x_d^2 \}, \end{aligned} \right\} \quad (3.16)$$

where  $Z P_{dk} x_d^2$  is the number of molecules formed per second by recombination of atoms, and  $\frac{1}{2} x_d$  is the number of molecules that are in the dissociated state (the initial number of molecules is taken to be unity). The number  $k$  denotes the level from which dissociation occurs.

The solution of the system (3.16) in the general case involves great difficulties, since this system describes two processes—the vibrational relaxation and the establishing of the equilibrium dissociation. As has been shown in Sec. 2, the relaxation times of these processes are different, and this makes it possible to simplify the solution of the problem decidedly. Since we are interested in the slow process, the establishing of the equilibrium dissociation, we can omit treatment of the fast process, the vibrational relaxation, and assume that at each time there is a certain quasi-stationary distribution of the molecules over the vibrational levels, which is determined by the value of the reaction rate at this same time.

The evolution of this quasi-stationary distribution (i.e., the slow process of the establishing of the equilibrium dissociation) determines the rate of dissociation.

The presence of these two different processes in the establishing of the equilibrium dissociation can be observed experimentally<sup>9,31,126</sup> (cf. Sec. 5.2).

By using these considerations we can rather simply find the distribution of the molecules over the vibrational levels during the process of dissociation and calculate the rate of dissociation  $k_{dis} = \frac{1}{2} dx_d/dt$ . It turns out<sup>39,57,58</sup> that the distribution function of the molecules in the upper vibrational levels during the process of dissociation differs markedly from the equilibrium distribution, and this has a decided effect on the process of dissociation. In reference 57 an explicit expression is found for the rate of dissociation; in the temperature range above the characteristic temperatures the expression is

$$k_{dis} = Z P_{av} \left( \frac{\hbar\omega}{D} \right) \left( \frac{D}{kT} \right)^{1.5} \exp \left( - \frac{D}{kT} \right), \quad (3.17)$$

where  $D$  is the dissociation energy,  $\hbar\omega$  is the largest vibrational quantum, and  $P_{av} \approx P_{k-1, k}$ .

For a comparison of Eq. (3.17) with experimental data it is necessary to take into account the influence



of the rotational and electronic degrees of freedom of the molecule. As has been shown in reference 39, the averaging of the rate constant  $k_{\text{dis}}$  over all the rotational states of the molecule being dissociated leads to the appearance of an additional factor  $g_{\text{rot}} > 1$  in the right member of Eq. (3.17). This is due to the fact that the effective dissociation energy of a rotating molecule is diminished owing to the action of centrifugal forces. The effect of the electronic degrees of freedom is included<sup>39</sup> by introducing a factor  $g_{\text{el}}$ , equal to the statistical weight of the stable electronic states that converge to the same dissociation energy  $D$ , in the right member of Eq. (3.17).

The formula (3.17) is derived on the assumption that the molecules that dissociate are a small impurity in a monatomic gas. An example of such a reaction is the dissociation of bromine,  $\text{Br}_2 + \text{A} \rightarrow 2\text{Br} + \text{A}$ , which has been studied in a shock tube at temperatures up to 2000°K.<sup>148</sup> The experimental rate constant of the dissociation is given by

$$k = 6 \cdot 10^{-2} Z_0 \left( \frac{D}{kT} \right)^{1.97} \exp \left( - \frac{D}{kT} \right), \quad (3.18)$$

where  $Z_0$  is the number of collisions per second experienced by a molecule in the ground state.

The theoretical value of  $k$  obtained in reference 39 is of the form

$$k \approx 5 \cdot 10^{-2} Z_0 \left( \frac{D}{kT} \right)^{1.5} \exp \left( - \frac{D}{kT} \right). \quad (3.19)$$

As is easily seen, the expressions (3.18) and (3.19) agree in order of magnitude.

Up to now we have confined ourselves to the discussion of the dissociation of diatomic molecules that form a very small impurity in a monatomic gas. The question arises as to how the rate of dissociation is changed if we replace the surrounding monatomic gas by dissociating diatomic molecules, i.e., consider dissociation in a system of one kind of molecule. In the dissociation of diatomic molecules in the medium of a monatomic gas the main process is the conversion of energy of translational motion of the monatomic gas into vibrational energy of the molecules. For dissociation in a system of a single gas the collisions between molecules lead not only to this process, but also to processes of transfer of vibrational and rotational energy. The first process has been studied in reference 49, the second in reference 40. The process of transfer of vibrational energy in collisions increases the dissociation rate constant. The physical reason for this effect is clear. As already stated, in the process of dissociation a quasi-stationary distribution of the molecules over the vibrational levels is established, which for the upper levels differs considerably from the equilibrium distribution. The rate of dissociation is determined by the rate at which molecules are brought from low vibrational levels to high ones. Because of their relatively high efficiency, processes of transfer of vibrational energy considerably increase the rate at which

molecules are got into the higher levels, and this leads to an increase of the rate of dissociation. A quantitative calculation of this effect shows<sup>49</sup> in the case of the "cut-off" oscillator model for the molecule that the rate of dissociation in the pure gas exceeds that in the medium of a monatomic gas by a factor  $\alpha = Q_{10}/P_{10}$  ( $Q_{10}$  is the probability of transfer of a vibrational quantum in a collision between oscillators in the ground and first excited states). Over the temperature range from 288°K to 1800°K the value of  $\alpha$  for  $\text{O}_2$  varies from  $5 \times 10^4$  down to 10.

Thus the effect of transfer of vibrations is effective mainly at low temperatures, and can be left out of account in the high-temperature region. Generally speaking the results obtained are of a qualitative character, since the use of the "cut-off" oscillator model does not take anharmonicity into account. In the case of polyatomic molecules, however, for which thermal dissociation occurs with a change of the multiplicity, the interaction potential along the bond being broken is well enough approximated by the cut-off harmonic oscillator. This is true in particular for the dissociation of  $\text{N}_2\text{O}$  into  $\text{N}_2$  and  $\text{O}$ . In this case the results obtained above can claim to give a quantitative description of the process.

The effect of processes of transfer of rotational energy on the dissociation rate constant has been studied in reference 40 for the case of the molecule  $\text{O}_2$ .

It was shown<sup>40</sup> that besides the process of conversion of translational energy into rotational energy in the collision of two molecules it is necessary to take into account also the simultaneous process of conversion of part of the rotational energy of the molecule not being dissociated into vibrations of the molecule that gets dissociated. Inclusion of this effect leads to a temperature-independent increase of the dissociation rate by a factor of about 20.\*

The experimental data (Sec. 6.4) show that the rate of dissociation in a single-gas system is larger than the rate of dissociation of the same molecules in a medium of a monatomic gas.

In giving the theory of thermal dissociation we have confined ourselves mainly to a survey of the work of Soviet authors. This is due to the fact that the approach to this problem in references 89 and 160 is subject to some objections. A detailed analysis of these papers is given in references 58, 40, and 41.

3.5. Establishing of the Equilibrium Degree of Ionization. Among all the relaxation processes considered in this review, the process of establishing the equilibrium ionization is the one that has been studied least. Existing experimental data<sup>139,147,153</sup> enable us to estimate the time for the establishing of the equilibrium ionization behind the front of a shock wave, but the physical processes that lead to this are not completely

\*More accurate calculations which we have made show that this estimate is much too high.

clear.<sup>80,153</sup> In the analysis of the vibrational relaxation and the dissociation the quantum-mechanical side of the phenomena has been sufficiently well known, and we have investigated the statistical picture of the phenomena.

The situation is much worse in the field of ionization kinetics. The main elementary processes that lead to ionization in shock waves are known: photoionization and ionization by electron and atomic collisions. There are, however, no complete quantum-mechanical calculations on these interactions. This is particularly true of the last-named mechanism. The main difficulty here is that the experimental values of the probabilities for electronic excitation and ionization in atomic collisions unambiguously indicate that these are nonadiabatic processes. The nature of the departure from adiabatic character is as yet not clear. An interesting attempt to interpret the lack of adiabatic character of these processes has been made in reference 44. The absence of quantum-mechanical calculations is naturally an obstacle to statistical calculations. Owing to this, at present the theory of the process of ionization in a shock front is mainly a set of qualitative arguments, closely associated with the experimental work.

The case that has been studied best is the kinetics of the ionization of argon.\* A monatomic gas is most favorable for the study of ionization, since there is no dissociation nor other chemical reaction, and the time for establishing the Maxwell distribution is much shorter than that for establishing the equilibrium ionization. In the experiments of Petschek and Byron<sup>153</sup> the speed of the shock waves corresponded to  $M \sim 18$ , and in equilibrium the gas behind the shock wave reached a temperature of 14000°K and was 25 percent ionized. The time for the establishing of equilibrium in this case was  $\sim 10 \mu\text{sec}$  (see Sec. 5.5).

The main elementary process leading to ionization is electron-atom collision. The cross section for this process is much larger than that for ionization by atom-atom collision, and therefore when there is a sufficient number of electrons the latter process can be neglected. This allows us to regard the process of ionization behind a strong shock wave in argon as occurring in two stages. In the second stage ionization by electron-atom collisions is the dominant process. The first stage will be discussed later. To determine the rate of ionization in the second stage we must calculate, first, the rate at which the electrons receive energy through elastic collisions, and second, the rate at which they lose energy in ionizing collisions. Then we must write the equation of balance and find the electron temperature and the rate of ionization. The proposed scheme of calculation is greatly simplified by the fact that in this case we can to a high degree of accuracy speak of the existence of an electron temperature and an atomic temperature. In

fact, owing to the great difference of their masses the electrons and atoms are energetically well isolated from each other; they can be regarded as weakly coupled systems. A calculation shows that an electron needs of the order of  $10^5$  collisions with atoms to lose its energy, but just one collision with another electron is enough for the establishing of the Maxwell distribution. Therefore there will be a Maxwell distribution, and consequently also an electron temperature, if for each  $10^5$  collisions of an electron with atoms there is at least one collision with another electron. When we take into account the difference of the effective cross sections for these collisions, the degree of ionization required for this is not more than  $10^{-8}$ . Generally speaking, the fact that the electrons and atoms are energetically isolated is not yet sufficient to assure the existence of electronic and atomic temperatures. In fact, the existence of negative and positive sources, which in this case are due to the disappearance of fast electrons and production of slow electrons in acts of ionization, can cause the quasi-stationary distribution in the system to differ from the equilibrium distribution. In the present case, however, this difference is not appreciable. As has been shown in reference 155, a negative source can lead to disturbance of the Maxwell distribution in cases in which it acts in the energy range  $E < 3kT$ . In the case in question  $E \sim 15.7 \text{ eV}$  (the ionization potential of argon), i.e.,  $E \gg kT$ . On the other hand, the production of slow electrons in the acts of ionization, though it can indeed lead to a local disturbance of the Maxwell distribution in the low-energy region, will not affect the tail of the Maxwell distribution, which determines the rate of ionization.

The calculation of the rate of ionization by this program has been made in reference 153. This paper also makes a comparison of the measured value of the time for establishing equilibrium with the calculated value of the rate of ionization. The results of the calculation show that it is necessary to assume the existence of an initial ionization amounting to about a tenth of the equilibrium degree of ionization of the gas. It is not clear what the processes are that lead to the appearance of the initial ionization, i.e., the processes in the first stage of the ionization. Attempts to explain the initial ionization by processes of thermal ionization in atom-atom collisions or of photoionization have been unsuccessful. Recently there have been attempts to explain the initial ionization by the existence of other processes.<sup>113a</sup> In particular, an attempt has been made<sup>5</sup> to explain the initial stage of the ionization by an effect of diffusion of resonance radiation through the front of the shock wave.

#### 4. FUNCTIONING OF A SHOCK TUBE

At the present time studies of the kinetics of non-equilibrium phenomena in gases at high temperatures are made mainly by means of shock tubes. A shock tube is a convenient device for producing a high tem-

\*The following presentation is based on reference 153.

perature in a gas, behind the shock front, under laboratory conditions. A feature of this device is that in the shock wave propagated in the tube the volume of heated gas being observed moves at high speed. Therefore the physico-chemical aspect of the phenomenon being studied is closely associated with the gasdynamical conditions of the flow of the gas; that is, on one hand the existence of the gasdynamic flow makes it possible to produce the high temperature, and on the other hand the development of the physico-chemical processes leads in a number of cases to considerable changes in the gasdynamical parameters of the flow. Therefore in setting up investigations of the kinetics of nonequilibrium phenomena in shock waves and in correctly treating the results obtained one needs a knowledge of the processes of formation and propagation of shock waves in shock tubes.

As is well known, the principle of operation of a shock tube is rather simple: the tube is divided by a diaphragm into two chambers—a high-pressure chamber, in which there is a compressed gas, and a low-pressure chamber, which contains the gas to be studied at a low pressure. After the rupture of the diaphragm, at some distance from the place the rupture occurs the flow of gas from the high-pressure chamber forms a shock wave, which propagates into the gas to be studied. At the same time a wave of rarefaction is propagated in the opposite direction in the high-pressure chamber.\*

For solving problems of physical kinetics it is desirable to have a shock wave moving with constant speed and accompanied by a one-dimensional and stationary flow of the gas. The obtaining of these conditions in an actually functioning shock tube requires a knowledge of the theory of the functioning of a shock tube. The simplified one-dimensional theory of the functioning of a shock tube that has been developed up to the present (cf., e.g., references 110, 152, 157) is based on a number of assumptions which to some extent idealize the mechanism of the processes in a shock tube. According to this theory it is assumed that the rupture of the diaphragm separating the high-pressure and low-pressure chambers occurs instantaneously, that the shock wave is formed instantly after the opening of the diaphragm, and that the wave then moves with constant speed. The flow in the tube is regarded as one-dimensional, and the gas as an ideal gas with constant specific heat. Effects of viscosity, thermal conductivity, and mixing of the gases at the surface of contact are neglected.

Actually, however, the processes in a real shock tube occur in a more complicated way. In this connection let us note only some well known aspects of the

\*A detailed description of the principles of operation of the shock tube can be found in the review articles 152, 181, and 151, and also in references 81 and 157. Especially strong shock waves are obtained in shock tubes in which a detonating mixture is used in the high-pressure chamber.<sup>146a</sup>

phenomena in shock tubes. First, it has been found<sup>185</sup> that the diaphragm separating the two chambers does not open instantaneously, but over a finite time interval. White,<sup>185</sup> working with a shock tube of square cross section  $82.5 \times 82.5$  mm, has shown (by observing the "clearance" in transmitted light) that under a pressure of 15 to 30 atm steel diaphragms of thickness 0.25–0.88 mm with cross scratches open over 90 percent of their area in 200  $\mu$ sec,\* and open entirely in 600  $\mu$ sec. As White states, the failure of the diaphragm to open instantaneously leads to the production of a whole train of compression waves, increases the distance at which the resulting shock wave is formed, and also in some cases leads to an increase of the intensity of the shock wave that is produced. On the other hand, the gradual opening of the diaphragm causes turbulence in the contact region. This mixing, accompanied by heating of the cold gas driving ahead and by cooling of the hot gas receiving the acceleration, has decided effects on the values of the thermodynamic and gasdynamic quantities in the end of the hot "plug" (i.e., the volume of gas included between the beginning of the front of the shock wave and the contact surface), and sometimes leads to a change of the speed of the shock wave.

Measurements of the variation of the speed of the shock wave along the tube showed that there are three regions in the shock tube: a speeding-up section, in which the speed of the shock wave is increasing, a section of uniform motion, in which the speed remains practically constant, and a section of damping of the wave, in which its speed drops (Fig. 1). It was found

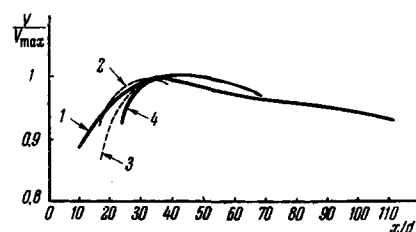


FIG. 1. Measured variation of speed of a shock wave along the tube, plotted against the ratio of the distance from the place the diaphragm broke to the diameter  $d$  of the tube.  $V_{\max}$  is the maximum speed of the wave. 1—oxygen,  $V_{\max} = 3.02$  km/sec<sup>26</sup>; 2—nitrogen,  $V_{\max} = 2.38$  km/sec<sup>61</sup>; 3—air,  $V_{\max} = 3.14$  km/sec<sup>61</sup>; 4—air,  $V_{\max} = 13.8$  km/sec.<sup>146a</sup>

that in a tube of inside diameter 50 mm with wave speed about 3 km/sec (in oxygen) the speeding-up section is 1.5 to 2 m long; in a tube 92 mm in diameter with wave speed 3.2 km/sec (in nitrogen and air)<sup>61</sup> this distance is 2.5 to 3 m. Even for a speed of 16.8 km/sec it was found in reference 146a that the wave gathers its speed over a distance of 3 m. White,<sup>185</sup> however, found that these distances increase with increase of the initial ratio of the pressures across the diaphragm before the experiment.

\*Translator's note: This is an error in quotation. White actually states that the opening was less than 10 percent in 200  $\mu$  sec.

The existence of a section in which the shock wave slows down is due to losses at the walls of the tube because of the development of a nonstationary boundary layer behind the front of the moving shock wave. Experiments have shown<sup>44,110</sup> that the speed of the contact surface systematically exceeds the calculated value of the speed of the flow behind the front of the shock wave, whereas according to the simplified one-dimensional theory the speed of propagation of the contact surface should not differ from the speed of the flow behind the front of the shock wave running on ahead. Dem'yanov<sup>11,12</sup> has succeeded in explaining this effect in terms of the development of a laminar boundary layer and in calculating the thickness of this layer by means of the relation

$$\delta = \sqrt{\frac{8\nu x}{V - \frac{13}{35}u}}, \quad (4.1)$$

where  $V$  is the speed of the shock wave,  $u$  is the speed of the flow,  $\nu$  is the kinematical viscosity of the gas behind the front of the wave, and  $x$  is the distance from the leading edge of the front. Bazhenova<sup>4</sup> has found experimentally the distribution of speeds in the flow between the leading edge of the front of the wave and the contact surface, for shock wave speed 0.85 km/sec in air, a case in which one cannot expect any appreciable influence of processes of physico-chemical change in the gas on the parameters of the flow. She found a gradual increase of the speed of the flow up to the end of the volume investigated; this is in qualitative agreement with Dem'yanov's calculations. Anderson<sup>68</sup> and Roshko<sup>161a</sup> have used simple arguments based on the balance of the masses of gas "flowing into" a given volume through the leading edge of the shock front and "flowing out" on account of retardation in a turbulent (at high pressures—Anderson) or laminar (at low pressures—Roshko) boundary layer to show that the distance from the leading edge of the front to the forward part of the contact surface in an actual tube is always smaller than according to the simplified one-dimensional theory; at sufficiently large distances from the place where the diaphragm broke the "plug" even begins to decrease in length. This result is in agreement with the experimental facts. There are also other papers<sup>91,104,142,105\*</sup> devoted to the analysis of the effect of the boundary layer on the flow of gas in a shock tube.

The effect of the boundary layer is especially evident in experiments in which the initial pressure is low and the tube diameter is small.<sup>104,161a</sup> For example, in experiments with a tube of inside diameter 33.4 mm Duff<sup>104</sup> found that with initial pressure  $p_1 = 0.5$  mm Hg the deviations from the one-dimensional type of func-

tioning of the tube are so large that this scheme cannot be used as a basis for describing the results. The author ascribes these deviations to the development of a laminar boundary layer which, under these conditions, occupies most of the cross section of the tube. Calculations made with the relation (4.1) show that in Duff's experiments the nominal thickness of the boundary layer at a distance of 25 cm from the leading edge of the shock front was 6–7 mm; in this case the boundary layer occupied about half the cross-sectional area of the tube. Consequently, according to these estimates one can regard the flow as one-dimensional and neglect the influence of the boundary layer only near the leading part of the shock front, in tubes of sufficiently large diameter, or when the initial pressure is sufficiently high. In each concrete case one can obtain quantitative estimates of the thickness of the laminar boundary layer by using relations derived in reference 161a.

A number of problems of the physico-chemical kinetics of the processes can be solved by studying the state of the gas behind the front of a wave reflected from the end of the tube, i.e., at a place where the heated gas must be at rest.<sup>2,14,111</sup> Many experiments and calculations<sup>56,140,175</sup> show, however, that one can do this only with some caution, since the homogeneity of the volume of gas behind the reflected wave is sometimes decidedly disturbed owing to the interaction of the reflected shock wave with the boundary layer that exists in the flow behind the incident wave. Therefore almost all of the most interesting results on nonequilibrium processes at high temperatures which we discuss below have been obtained from studies of the state of the gas behind the front of the incident shock wave.

Thus, the most suitable conditions for observing nonequilibrium phenomena in a shock tube are as follows:

1. The studies are made at such a distance from the diaphragm that the process of formation and speeding-up of the shock wave have been completed and the shock wave is moving with constant speed.
2. The part of the flow behind the leading edge of the shock front must be sufficiently small in comparison with the entire distance from the front to the contact surface, for otherwise difficulties arise in finding the causes of changes in the different measurable quantities.
3. The tube diameter and the initial pressure must be large enough so that the damping of the shock waves and the boundary layer do not have much effect on the parameters of the flow.

It is assumed that under these conditions the flow in the region observed behind the front of the wave will be a one-dimensional stationary flow; therefore one can apply to this section of the flow the laws of conservation of mass, momentum, and energy in integral form, with the possibility of physico-chemical

\*We have obtained the references to these papers from a bibliographical index "Shock Waves," prepared for publication by the Institute of Mechanics of the Academy of Sciences of the U.S.S.R.

changes properly taken into account (cf. e.g., reference 124, Sec. 6 of Chapter 11).

## 5. EXPERIMENTAL METHODS FOR STUDYING THE STATE OF A GAS IN A SHOCK WAVE

The experimental study of the nonequilibrium phenomena that we have described depends on the observation of the change with time of certain of the parameters that characterize the state of the gas in a shock wave. Therefore a main quantity to be measured is the time during which a change of the composition, the density, the temperature, or some other characteristic of the state of the gas occurs in the process of establishing equilibrium. Consequently, a basic criterion of the suitability of a method for studying the nonequilibrium phenomena is the time resolution of the apparatus; naturally the method to be used must also be sufficiently sensitive to changes of the characteristics of the medium. There have by now been developed quite a number of experimental methods, which have made possible the accumulation of much factual material from studies of the processes of excitation of rotations and of molecular vibrations, changes of occupation of electronic levels, dissociation, and ionization, in the gas behind the front of a shock wave as it is propagated along a shock tube. A decisive role has been played by optical methods, which have made it possible to get high time resolving power (fractions of a microsecond) without appreciable effect on the object being observed.

5.1. Measurement of the Density of the Gas. The density of the gas is one of the main parameters characterizing both the thermal and the gasdynamic state of the medium. It is by studies of the distribution of the gas density behind shock wave fronts that the main results on the excitation of rotations and vibrations and on the dissociation of molecules have been obtained.

Let us first discuss a precision method for measuring the density distribution in the front of a shock wave developed by Hornig, Cowan, Greene, and Anderson (a bibliography of the papers of these authors can be found in reference 69). The apparatus devised by these authors measures the coefficient of reflection of light from the surface of the leading edge of the shock wave. An intense parallel light beam (in the first experiments from a carbon arc, in later ones from a tungsten lamp, which was found to be better because of its stability) was incident at the angle  $\theta$  (in various experiments the value of  $\theta$  ranged from  $62^\circ$  to  $82^\circ$ ) on the surface of the leading edge of the shock front as it went past observation windows, and then the reflected part of the light fell on a photomultiplier. The experimentally measured value of the reflection coefficient (amounting to  $10^{-5}$ – $10^{-7}$ ) was compared with calculated values found from definite assumptions<sup>101</sup> about the density distribution (which is connected with the index of refraction by well known

relations) in the wave front. The expression found most suitable for correlating the results is

$$\rho = \rho_1 + \frac{\rho_2 - \rho_1}{1 + \exp\left(-\frac{4x}{L}\right)}, \quad (5.1)$$

where  $\rho_1$ ,  $\rho_2$  are the values of the density of the gas before and after the passage of the leading front of the wave, and  $L$  is the effective thickness of the wave front,

$$L = \frac{\rho_2 - \rho_1}{\left(\frac{d\rho}{dx}\right)_{\max}}$$

Values of the quantity  $L$  were obtained for a number of gases (Ar, N<sub>2</sub>, O<sub>2</sub>, CO, CO<sub>2</sub>, N<sub>2</sub>O, Cl<sub>2</sub>, HCl, and others) for shock-wave speeds a little above the speed of sound in the undisturbed gas (Table I).

**Table I.** Measured thickness  $L$  of shock-wave front (in units  $10^{-5}$  cm), as function of the number  $M$ , for initial pressure  $p_1 = 1$  atm and temperature  $T_1 = 300^\circ$  K

M	Gas						
	N <sub>2</sub>	O <sub>2</sub>	CO	N <sub>2</sub> O	CO <sub>2</sub>	HCl	Ar
1.08							28.8
1.23	8.5	9.9	7.4	6.2	5.0	6.2	8.5
1.37	5.7	7.4	6.0	4.5	4.2	5.0	6.0
1.55	3.3	4.1	3.7	2.9	2.5	2.0	4.2

A number of interesting results have been obtained by measuring the density gradient in the flow behind the front of a shock wave by means of the Toepler schlieren method, which is widely used in gas-dynamical research.<sup>64</sup> This method has been used photographically by Glick and Wurster to study the process of dissociation of oxygen behind the front of a shock wave in a shock tube,<sup>112</sup> and photoelectrically by Resler and Scheibe to study the process of vibrational excitation in CO<sub>2</sub> and other gases.<sup>158,159</sup> A fundamental treatment of the principles of operation of a number of schlieren schemes and a derivation of the formulas required in processing the results is given in papers by Schardin, in particular in reference 167. Naturally the photoelectric method of registration makes it possible to get higher resolution in time.

The most complete studies of the density distribution behind the front of a shock wave when there are nonequilibrium effects have been made with interferometers,<sup>76,77,117,143,144,174,156</sup> which, as is well known, give direct measurements of the density of the gas. For this purpose one includes the working section of a shock tube in one arm of an interferometer of the Mach-Zander type<sup>64</sup> (a compensator is placed in the other arm). In several researches, reference 117 etc., instantaneous pictures were taken of the density distribution behind the front of a shock wave (Fig. 2); in other work<sup>76,156</sup> the photographic-sweep method was

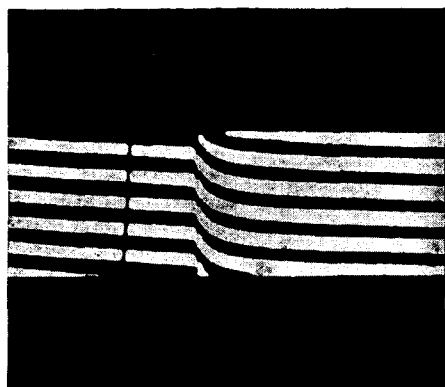


FIG. 2. Interferogram of the density distribution in a shock wave propagated with speed 2 km/sec in a mixture of 66 percent  $O_2$  and 34 percent  $N_2$ ; the initial pressure was  $p_1 = 21$  mm Hg.<sup>77</sup>

used: the interference fringes were projected on the slit of a photographic-sweep camera. In this case the shift of the bands is measured as a function of the time of passage of the heated gas past the observation windows.

Systematic studies made with interferometers by different experimenters, using different tubes and working under different conditions, have established the fact that when nonequilibrium processes are occurring in pure gases or in mixtures in which the diluting gas is an inert gas the density behind the shock front gradually increases and approaches the equilibrium value,\* i.e., the value obtained from the integral conservation laws for mass, momentum, and energy for the equilibrium excitation of the internal degrees of freedom of the molecules and the equilibrium dissociation and ionization of the atoms and molecules.

As the initial pressure in the low-pressure chamber of the tube is decreased the sensitivity of the schlieren and interferometer methods falls. Therefore for the study of the structure of shock waves at low pressures a method has been developed for measuring the density distribution in the gas in a shock tube by means of the scattering of an electron beam sent through the gas perpendicular to the axis of the tube.<sup>74,104,106,182</sup> In these experiments an electron beam produced by an electron gun was accelerated by a potential of 10–40 kv and entered the working section of the tube through a thin platinum foil. The registering device was a photomultiplier with a scintillation converter. In the energy range chosen the electrons are mostly only elastically scattered; the scattering coefficient depends on the energy of the electrons, the atomic weight, and the density of the gas. Thus measurement of the attenuation of the beam during the time of passage of the shock wave past the

\*In mixtures such as air one sometimes observes values of the density above the equilibrium value, owing to the simultaneous occurrence of a number of processes at different rates (cf., e. g., reference 156).

point in question makes it possible to obtain the density distribution of the gas; the resolving time of such an apparatus is less than 0.5  $\mu$ sec. Experimenting with argon at initial pressure 0.5 mm Hg, Ballard and Venable determined the thickness of the front of a shock wave in argon and found that for wave speeds  $M = 3, 4,$  and  $5.8$  the zone of redistribution of the translational motions of the atoms is respectively 4.4, 3, and 8.5 times the mean free path. Under the same conditions, but over a wider range of speeds ( $M = 1.6 - 7$ ), Duff and Webster<sup>106</sup> found that the thickness of the wave front has a minimum at  $M = 3$ , equal to 6.5 times the mean free path for the conditions in front of the wave, and then slowly increases for stronger shock waves.

Studies of the density distribution of the gas behind the front of a shock wave have also been made by measuring the absorption of soft (long-wave) x-radiation.<sup>93,129,132</sup> Knight and Venable<sup>132</sup> assume that the absorption of soft x-rays in a heavy inert gas is described to good approximation by the exponential law

$$I_d = I_0 e^{-\mu_0 d}, \quad (5.2)$$

where  $I_0$  and  $I_d$  are the intensities of the incident beam and the beam after passage through a thickness  $d$  of the gas, and  $\mu$  is the absorption coefficient calculated per unit length and unit density. Then a determination of the absorptive power  $\alpha = 1 - (I_d/I_0)$  gives a measurement of the density of the gas. The apparatus uses pulsed x-ray tubes at voltages up to 20–30 kv, with copper anodes and tungsten targets (also chromium and copper targets), which give a continuous spectrum. The tubes are mounted directly on the working section of the shock tube; the windows are beryllium foil of thickness less than 0.25 mm. The detector is a photomultiplier used with a scintillator; the resolving time is 0.2–1  $\mu$ sec. Xenon is the most effective absorbing gas; the value of  $\mu$  for the chosen operating voltage is found by a static calibration, in which the tube is filled with xenon to various pressures. Chesik and Kistiakowsky<sup>93</sup> have used xenon to dilute other gases to be studied ( $N_2, O_2, H_2, CH_4, C_2H_4, C_2H_6$ ), and have thus measured the vibrational relaxation time and the relaxation time for dissociation behind the fronts of shock waves.

5.2. Measurement of the Concentrations of the Components of the Gas. Studies of the distribution of the concentrations of the components of a gas behind the front of a shock wave by means of absorption spectra have been very successful. In this way results have been obtained bearing on the dissociation of  $N_2O_4$ ,<sup>90</sup>  $I_2$ ,<sup>82,83</sup>  $Br_2$ ,<sup>84,148</sup>  $O_2$ ,<sup>26,86</sup> and  $H_2O$ ,<sup>75</sup> and on the excitation of vibrations in  $NO$ <sup>181</sup> and  $O_2$ .<sup>9,31</sup>

The method is rather simple: Light from a source (an arc or a lamp) passes through the shock tube perpendicular to its axis; the required part of the spectrum is then singled out by a light filter or a spectrograph. The light pulse is converted by a photomulti-

plier into an electrical signal, which goes to an oscilloscope. The signal level is measured before and after the passage of the front of the shock wave; this makes it possible to get the distribution of the absorbing power  $\alpha$  behind the front of the shock wave. As is well known, for the continuous spectrum the registered absorbing power is connected with the absorption coefficient by the relation

$$\alpha = \frac{\int \psi (1 - e^{-k_\nu l}) d\nu}{\int \psi d\nu}, \quad (5.3)$$

where  $\psi$  is a function characteristic of the apparatus, and  $k_\nu$  is the absorption coefficient, which depends on the concentrations  $N_i$  of the absorbing molecules of types  $i$  in unit volume, the oscillator strengths  $f$  for the corresponding optical transitions, and the frequency  $\nu$ . In cases in which  $k_\nu$  is only weakly dependent on  $\nu$  (in the observed range  $\Delta\nu$ ) the relation (5.3) can be simplified, and reduces to  $\alpha = 1 - \exp(-\kappa N_i l)$ . The quantity  $\kappa$  (the absorption coefficient computed for unit length and unit concentration) is usually found experimentally, for example, for iodine and bromine in the regions of 4870 Å and 4360 Å,<sup>82-84</sup> and for bromine in the region of 4390 Å.<sup>148</sup> In reference 86 the continuous absorption spectrum of molecular oxygen (the Schumann-Runge continuum) was used in the region of 1470 Å. It is harder to determine the relation between  $N_i$  and  $\alpha$  in the case of a band spectrum,<sup>30,161</sup> when the lines making up the spectrum are reabsorbed and overlap; here one can only rely on experimental measurements of the function  $\alpha(N_i, T)$  at points of the flow corresponding to an equilibrium state of the medium,<sup>10</sup> i.e., far from the front of the wave. Knowing the character of the function  $\alpha(N_i, T)$ , one can get an idea of the cause of the change of the absorbing power near the front of the wave, and by measuring  $\alpha$  can find the time for establishing equilibrium.

The superiority of absorption-spectroscopic methods shows itself in studies of the processes in complex mixtures of gases, for example such mixtures as air. From studies of the character of the absorption of ultraviolet radiation behind shock fronts in air<sup>10,29</sup> it has been possible to show that near  $\lambda = 2200$  Å the absorption of the light is mainly determined by transitions from the fourth and fifth excited vibrational levels of the ground electronic state  $X^3\Sigma_g^-$  to the state  $B^3\Sigma_u^-$  of the oxygen molecule (Schumann-Runge bands). The dependence of the absorbing power on the temperature and the concentration of molecular oxygen was found. This made it possible to study the process of dissociation of the oxygen in air<sup>10,28</sup> (Fig. 3).

Another virtue of this method is the possibility of separating the zones for vibrational relaxation and for dissociation at high temperatures, since in this case the excitation of vibrations increases the absorbing power and dissociation decreases it (Fig. 4). This makes it possible to measure the zone of excitation

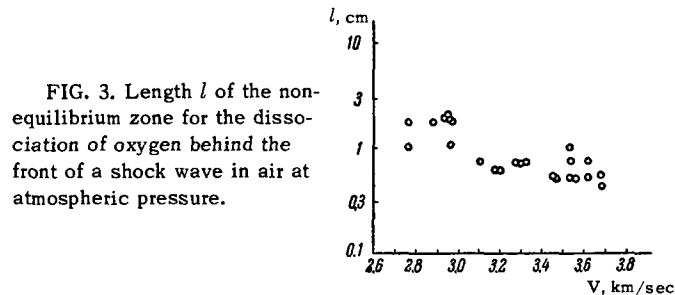


FIG. 3. Length  $l$  of the nonequilibrium zone for the dissociation of oxygen behind the front of a shock wave in air at atmospheric pressure.

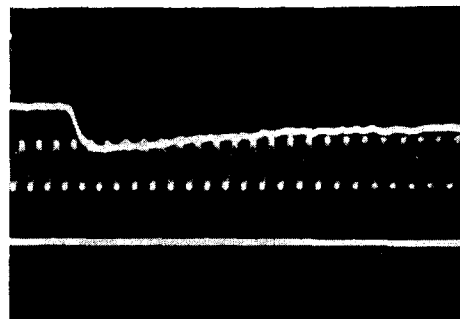


FIG. 4. Oscillogram of the distribution of absorbing power in a shock wave propagated at speed 3.1 km/sec in oxygen at initial pressure  $p_1 = 1.5$  mm Hg.

of vibrations before the beginning of dissociation; in this way the relaxation time of the vibrations of the  $O_2$  molecules has been measured up to temperatures  $T = 9 - 10$  thousand degrees.<sup>9,31</sup> The characteristic time for the dissociation of the  $O_2$  molecules was measured simultaneously; this showed that in a shock wave this time is much longer than the vibrational relaxation time (Table II). In these experiments the resolving time of the registering devices was less than  $0.05 \mu\text{sec}$ .

As is well known, much can be accomplished in the study of the kinetics of gas reactions by using a source of illumination that gives the line spectrum of the gas components that are being studied.<sup>18,21</sup> This method has also been successfully applied in work with a shock tube, in a study of the kinetics of the decomposition of water vapor at temperatures  $T = 2400 - 3200^\circ\text{K}$ ;<sup>75</sup> the authors observed the absorption in the OH bands in the region of 3095 Å.

**5.3. Measurement of the Intensity of Radiation.** A number of authors have also used measurements of the emitting power of the gas behind the front of a shock wave to study relaxation processes at high temperatures.<sup>163,164,190,86,153,186,73,etc.</sup> By now there have been a great many studies of the luminosity of gases in shock waves produced in shock tubes. The spectral composition and time characteristics of the luminosity have been studied in air,<sup>127,128</sup> oxygen,<sup>86</sup> argon,<sup>154,186,66</sup> xenon,<sup>162,66,67,125,164,113a</sup> krypton, and in mixtures of krypton with hydrogen<sup>32</sup> and with other gases.<sup>114,99,109,126</sup>

The very first researches showed that the spectra of the luminosity contain a number of lines from im-



**Table II.** Vibrational relaxation time of  $O_2$  ( $\tau_{vib}$ ) and characteristic time for dissociation of  $O_2$  ( $\tau_{dis}$ ) in a mixture of 21 percent  $O_2$  and 79 percent Ar ( $p_2$  is the pressure behind the front of the wave)

$V$ , km sec	$p_2$ , atm	$\tau_{vib}$ , $\mu$ sec	$\tau_{dis}$ , $\mu$ sec	$\frac{\tau_{dis}}{\tau_{vib}}$	$V$ , km sec	$p_2$ , atm	$\tau_{vib}$ , $\mu$ sec	$\tau_{dis}$ , $\mu$ sec	$\frac{\tau_{dis}}{\tau_{vib}}$
2.28	0.65	2.6	21.2	8	2.57	0.83	1.8	24.8	14
2.33	1.36	1.8	26.8	15	2.64	0.88	1.1	13.8	13
2.34	3.4	0.8	10.6	13	2.70	1.84	0.7	13.8	20
2.36	3.5	0.7	17.8	25	2.78	0.97	0.5	7.5	15
2.38	1.4	1.3	19.5	15	2.86	1.02	0.4	6.3	16
2.44	0.75	1.1	8.4	8	3.09	1.18	0.4	5.8	14

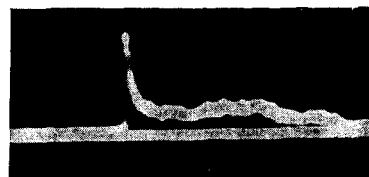
purities which have low ionization potentials (sodium, calcium, and so on); even after careful purification it is hard to get rid of the presence in the spectrum of lines such as the sodium D lines. It turned out that in a number of cases the luminosity observed in the front of the shock wave is due to the radiation from impurities such as  $C_2$  and  $CN$ , excited molecules of which are formed very quickly (in a time less than  $1 \mu\text{sec}$ ) in the heated gas from impurities containing carbon; in such cases the partial pressure of impurities in the gas before the front of the shock wave does not exceed  $10^{-2} - 10^{-1}$  mm Hg.<sup>92,99</sup> This fact sometimes has to be taken into account in analyzing results, in order not to come to false conclusions about the development of the processes in the main gas (Fig. 5).

In studying the development of the processes behind the front of the wave it is necessary to know the time characteristics of the distribution of luminosity of a particular spectral composition. Therefore experiments are most often done with monochromators or with photoelectric radiation detectors.\* The signal then goes, as usual, to a pulse oscillograph. In this way Windsor, Davidson, and Taylor<sup>190</sup> have measured the vibrational relaxation time of the CO molecule, by registering the distribution of the infrared radiation in the wavelength range 2–2.8 (which corresponds to transitions from the second excited vibrational level of the CO molecule, and also to some other transitions.<sup>103</sup> The detector for the infrared radiation had an equilibrium time of about  $30 \mu\text{sec}$ ; thus it was possible to measure only the rather long vibrational relaxation times (behind shock waves reflected from the end of the shock tube).

By measuring the intensity distribution of the infrared radiation of NO in the region around  $5.3 \mu$ , Allport has studied the kinetics of the formation of NO behind the front of a shock wave in air<sup>73</sup> and the mechanism of the decay of the NO molecules behind the front of a shock wave in pure nitric oxide.<sup>72</sup>

Rates of dissociation of  $N_2$ ,  $O_2$ , and air have been measured by studying the radiation emitted by the heated gas as a function of the time.<sup>86,87</sup> A two-channel

\*Gloersen<sup>113a</sup> has used a television camera with an orthicon to register the development of the spectrum in time.



**FIG. 5.** Oscillogram of the distribution of luminosity ( $\lambda = 2600 \text{ \AA}$ ) in a shock wave propagated at a speed of 3.8 km/sec in oxygen contaminated with gasoline; initial pressure 1.5 mm Hg.

monochromator was used, which singled out portions of the spectrum of widths 33 and 66  $\text{\AA}$ ; measurements were made near  $\lambda = 3410, 3890, 3920,$  and  $4780 \text{ \AA}$ . It was found that the intensity of the observed radiation has a maximum immediately behind the front of the wave; the signal level then falls off exponentially, right down to the equilibrium value. Despite the fact that the intensity of the radiation changes markedly with the wavelength, the characteristic relaxation times measured for various wavelengths were practically identical. The decrease of the radiation can be connected with the drop of temperature behind the front of the wave during the process of dissociation. It is well known that the intensity of the radiation is proportional to the population of the excited electronic state. Therefore the measured relaxation time corresponds to two processes going on in parallel—the excitation of electronic levels and the dissociation of molecules. Consequently, in a given case this method permits measurement of only an upper limit on possible values of the relaxation time of a particular process.

Studies of the mechanism of excitation of electronic levels are described in papers by Roth and Gloersen,<sup>184,182,113a</sup> who examined the intensity distribution of the luminosity in shock waves propagated in xenon with speeds  $M = 8 - 11$ , at initial pressures 0.5–4 mm Hg. In experiments done by Gloersen the radiation was registered at five points along the shock tube, separated by distances of 40 cm, and also the spectrum of the luminosity was photographed over the range 3000–10,000  $\text{\AA}$  at a distance of 45 cm from the end of the tube. The values of the delay time of the luminosity, as found by Gloersen, are shown in Fig. 6. It was



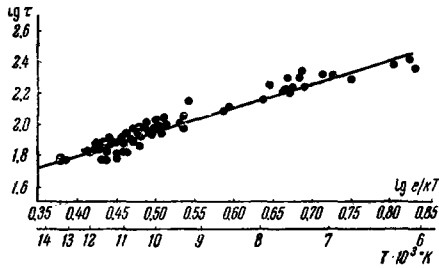


FIG. 6. Delay time ( $\tau$ ,  $\mu$  sec) of luminosity in xenon, as a function of the reciprocal of the temperature immediately behind the shock front (in eV).<sup>113a</sup> The Kelvin absolute temperature is shown on the lower scale.

found that this time does not depend on the initial pressure of the gas; its dependence on the speed of the shock wave is such that it cannot be explained without taking into account photoelectric emission from the walls of the tube before the shock front. The possibility of an effect of the geometry of the shock tube on the process of excitation of the luminosity is pointed out.

In studies of the effects of small amounts of air and other gases added to xenon, Roth<sup>163</sup> used the distribution of emission behind the shock front in the system of violet bands of  $\text{CN}(\text{B}^2\Sigma^+ - \text{X}^2\Sigma^+)$ , in the region 3871 and 3883 Å, to obtain results on the deactivation of vibrational levels of the CN molecule at temperatures 6300 – 9550° K.

The character of the excitation of the electronic levels of He I at 5876 Å and He II at 4686 Å in a shock wave in helium at a speed of 20 km/sec has been studied in reference 187; high resolution in time (less than 0.05  $\mu$ sec) was attained in this work. In reference 183 emission of the line He I 5687 Å was detected in the gas before the arrival of the shock wave.

A study of the distribution of continuous radiation behind the front of a shock wave in argon in the regions 4680, 4970, and 5000 Å has been made by Petschek and Byron.<sup>153</sup> They also used the photoelectric method of registration; the results were used to measure the distribution of concentration of electrons and to construct a picture of the process of thermal ionization behind the front of a shock wave (see Sec. 3).

In some papers photographic methods have been used to register the appearance of radiation behind the front of a shock wave by photographing the spectrum on a moving film. For example, Niblett and others<sup>147</sup> have made an attempt to measure the time of establishing of the equilibrium ionization behind a shock wave in air; it must be remarked that the results they obtained are very roughly approximate.

**5.4. Measurement of the Temperature of the Gas.** Measurement of the temperature of the gas behind the front of a shock wave in a shock tube is a matter of great interest. A great many papers have been published by authors who have measured the temperature of the gas by pyrometric methods—observations of the emission and absorption of light in the lines of

impurities mixed with the main gas (impurities used were sodium, barium, indium, chromium, etc.).<sup>54,55 59-62,27,96-98</sup> The basis of these methods are the assumptions that there is thermal equilibrium between the excited impurity atoms and the main gas, Kirchhoff's law can be applied, and that radiative equilibrium is only slightly disturbed by the emergence of radiation from the heated gas. In cases in which these assumptions hold, simultaneous measurements of the distributions of emitting and absorbing powers of the gas behind the front of a shock wave make it possible to determine the temperature distribution in accordance with the laws of optical pyrometry.

For this purpose two channels (one above the other) are made in the working section of the tube, perpendicular to its axis. Through the first channel light is sent across the tube from an external source placed behind the tube, so that the absorbing power of the gas can be measured; the radiation from the gas in the tube also comes into this channel. Only the light from the gas itself comes through the second channel, which serves for the measurement of the emitting power. The light then goes through a monochromator, which singles out from both channels identical portions of the spectrum (in the neighborhood of a wavelength  $\lambda$ ) these portions of the light fall on two photomultipliers; the signals are registered by means of a two-beam pulse oscillograph. By using various types of calibration of the registered signals in terms of a standard temperature source, one can get several modifications of the method for measuring temperatures:

a) Direct calibration of the proper radiation of the gas, by replacement of the working section of the tube by a standard straight-filament lamp. Assuming the validity of the Wien law, we get for the unknown temperature  $T_x$ , for  $T_x < 6000^\circ$  K, the formula

$$T_x = T_s \left[ 1 - \frac{\lambda T_s}{C_2} \ln \frac{m}{1 - \frac{\beta I''}{I'_n} \alpha_{\lambda \lambda_0}} \right]^{-1}, \quad (5.4)$$

where  $T_s$  is the brightness temperature of the standard (for the wavelength  $\lambda_0$ ),  $I'$  and  $I''$  are the amplitudes of the signals in the first and second channels,  $\beta$  is the coefficient for reducing the sensitivity of the second channel to the sensitivity of the first,  $I'_n$  is the amplitude of the signal from the source of illumination,  $m$  is the ratio of the signals in the measurement and the calibration ( $m = \beta I''/I'_k$ ),  $\alpha_{\lambda \lambda_0}$  is a coefficient that corrects for the change of the brightness temperature when we go from  $\lambda_0$  to  $\lambda$ , and  $C_2$  is the second constant in the Planck formula.

b) Calibration of the source of illumination in terms of a temperature  $T_n$ , by replacement of the source by a standard filament lamp (generalized method of reversal of spectral lines). Then under the same conditions, for a source of illumination operating on constant current, we have

$$T_x = T_n \left[ 1 + \frac{\lambda T_n}{C_2} \ln \frac{I'}{\beta I''} \right]^{-1}, \quad (5.5)$$

where  $\varphi$  is the coefficient for the losses in the optical system from the source of illumination to the inside surface of the shock tube, and  $T_n$  is the brightness temperature of the source, determined from the relation

$$T_n = T_s \left[ 1 - \frac{\lambda T_s}{c_2} \ln n \cdot \alpha_{\lambda \lambda_0} \right]^{-1} \quad (5.6)$$

( $n$  is the ratio of the signals from the source of illumination and the standard).

The authors of other papers<sup>96-98</sup> have used for measuring the temperature of the gas in a shock tube the ungeneralized (ordinary) method of line reversal, which requires that "reversal" of the lines be attained—that the signal from the source of illumination be brought to equality with that from the luminosity of the gas in the tube. An advantage of this method is that only one channel of registration is needed; a shortcoming is that it is possible to measure the temperature only at the points at which "reversal" is observed.

Let us examine the basic assumptions associated with the use of pyrometric methods for measuring the temperature of the gas, and the possibilities of using these methods for the study of nonequilibrium phenomena. Naturally one cannot rely on the existence of thermal equilibrium between the main gas and the excited impurity atoms at points immediately behind the front of a shock wave; a certain time interval is necessary for the evaporation, dissociation, and excitation of the impurity atoms, which are present in the gas mainly in the form of salts. For example, for sodium impurities in nitrogen and air this time is 10–20  $\mu\text{sec}$ <sup>61,96</sup> at  $T \sim 4000^\circ\text{K}$ , and even goes as high as 50  $\mu\text{sec}$ .<sup>98</sup> This severely limits the possibilities of using these methods for the study of nonequilibrium phenomena behind the front of a shock wave. As has been shown in references 36 and 65, the validity of Kirchhoff's law for the observed radiation depends on the existence of a Boltzmann distribution of the atoms over the electronic levels, and the time for establishing this distribution is determined by the number of collisions of the impurity atoms with other particles and on the cross section for excitation. On the other hand, as Biberman<sup>6</sup> has shown, there can be deviations from the Boltzmann distribution over the levels, owing to the passage of radiation beyond the space occupied by the heated gas (in our case, the heated "plug" between the leading edge of the shock front and the surface of contact). According to reference 6 the emergence of radiation from the "plug" leads to deviations from Kirchhoff's law and to a lowering of the measured temperature relative to the true value; the size of the deviation  $\Delta T$  increases with decrease of the ratio of the probability of collisions of the second kind to that of optical deexcitation, and with decrease of the optical thickness. Recalling the known values of the probability of collisions of the second kind<sup>8,37,51</sup>

between atoms of Na and a number of other metals and electrons, and between inert-gas atoms and molecules of  $\text{N}_2$ ,  $\text{H}_2$ , and so on, we can conclude that for  $T < 5000^\circ\text{K}$  the value of  $\Delta T$  will be largest in the case of temperature measurements in a monatomic gas, because of the smallness of the cross section for excitation of impurity atoms in collisions with other atoms; in this case the emergence of radiation wins out over the excitation. This finds confirmation in the experiments;<sup>62,97,99</sup> in the case of measurement of the temperature of argon by means of the line Ba II 4554 Å<sup>62</sup> with a pressure of about 0.5 atm in the plug, the measured temperatures were more than  $1000^\circ$  below the calculated values; the discrepancy becomes smaller when the pressure is increased. Assuming that the temperature calculated from the Hugoniot adiabat for shock waves in argon is the true value, the authors of reference 59 obtained for the effective cross section for excitation of Ba II ions by collisions of the second kind with argon atoms at  $T = 4000 - 5000^\circ\text{K}$  the value  $4 \times 10^{-17} \text{ cm}^2$ . Studies of this sort open up the possibility of using shock tubes to measure the probabilities for excitation of individual electronic levels under various conditions.

A different picture is observed in experiments with diatomic gases: the cross section for excitation of the lines of impurity atoms in collisions with vibrationally excited molecules is so large that the quantity  $\Delta T$  is negligible. Therefore in measurements of the temperature behind the fronts of shock waves propagated in nitrogen and air at speeds 1.9–4.3 km/sec Faizullof, Sobolev, and Kudryavtsev<sup>60,62</sup> found that after thermal equilibrium is established between the excited impurity atoms and the main gas, at pressures 0.1–4 atm, the measured temperature (within experimental error,  $\pm 70^\circ$ ) agrees with the calculated values obtained from the integral conservation laws on the assumption of complete thermodynamic equilibrium.

The large cross section for excitation of sodium atoms by vibrationally excited  $\text{CO}_2$  molecules has been used by Hurle and Gaydon<sup>126</sup> for a determination of the relaxation times of carbon dioxide for vibrations and dissociation near  $2500^\circ\text{K}$ .

Because of the previously noted shortcoming, this method for measuring the temperature cannot be used for studying conditions near the precise front of the shock wave, where it would be very desirable to know the temperature distribution in studying nonequilibrium phenomena in a given gas.\* To overcome this handicap it is necessary to measure the temperature by the emission and absorption of light in the main gas itself, and

\*These same shortcomings also affect other methods for measuring the temperature of a gas through impurities—the method of the relative intensities of lines (Ornstein method) and the method of measurement of  $T$  from the intensity distributions in molecular bands.<sup>55</sup> The method of temperature measurement by the rate of propagation of ultrasonic vibrations in a gas in a shock tube<sup>141</sup> also has unsatisfactory time resolution.

not in added impurities, as has been done in a paper by Model',<sup>38</sup> this is possible, however, only at sufficiently high temperatures. Under these conditions use is sometimes made of a method for measuring  $T$  from the absolute value of the total emission in one or another line of the main gas.<sup>138,137</sup> In this way one can get extremely high resolving power in time (0.05  $\mu$ sec and shorter), which is very important in the study of nonequilibrium phenomena.

#### 5.5. Measurement of the Concentration of Electrons.

Interest in the study of the kinetics of thermal ionization has caused the development of a number of methods for measuring the concentration of electrons behind the front of a shock wave. Essentially these are extensions of already known ways of studying gas-discharge plasmas; they include probe, spectral, magnetic, and radio-frequency methods.

One of the earliest methods for studying a plasma is the well known probe method of Langmuir. The first attempts to apply this method to the measurement of the electric conductivity of argon behind the front of a shock wave in a shock tube<sup>135</sup> were not successful; the values obtained for the electric conductivity were considerably lower than the calculated values; this depression of the values could not be unambiguously interpreted because of the presence of a cold boundary layer at the measuring probe. Further improvements in the method (use of a "point" working surface at the end of a thin sharp probe, and so on) made it possible to get some results which correlated the variation of the potential  $\varphi$  of the probe with the changes of the state of the gas surrounding it.<sup>153</sup> It was found experimentally that on passage of the shock front (in argon) the potential of the probe shows a sharp jump; the signal then remains constant (which corresponds to small values of the electron concentration  $N_e$  behind the front of the shock wave, when  $\varphi$  is constant), and thereafter it begins to increase, since for sufficiently large values of  $N_e$

$$\frac{1}{T_e} \frac{d\varphi}{dx} \sim \frac{d \ln N_e}{dx} \quad (5.7)$$

where  $T_e$  is the electron temperature and  $x$  is the distance from the leading edge of the shock front. Finally the voltage at the probe becomes constant again; the authors of reference 153 identify this instant with the establishing of the equilibrium state. In this way the time for establishing the equilibrium ionization behind the front of a shock wave in argon has been measured over the range  $M = 11 - 20$ .

The probe method has made it possible to detect the presence of electrons before the passage of a shock wave in argon at  $M = 8 - 12$ ;<sup>184</sup> measurements by means of external electrostatic probes in pure xenon have indicated the presence of charges in the gas 400  $\mu$ sec before the arrival of a shock wave.<sup>113,113a</sup>

In reference 153 the distribution of  $N_e$  was examined through the change of intensity of the continuous

radiation, on the assumption that the luminosity is due to the recombination spectrum and that its intensity is proportional to the square of the electron concentration. Then for the fractional rate of change with time of the intensity  $I$  of the radiation behind the shock front we have

$$\frac{1}{I} \frac{dI}{dt} = \frac{2}{N_e} \frac{dN_e}{dt} \quad (5.8)$$

These data have also made it possible to estimate the time for establishing ionization equilibrium; the authors state that impurities have a considerable effect. In their latest work White and Alpher<sup>186</sup> studied the luminosity of argon behind a shock front (at Mach numbers 10 - 19) and found that the maximum intensity of the luminosity in the neighborhood of 4120 Å is proportional to the 1.6 power of the equilibrium electron concentration [over a range of concentrations  $(1.7 - 17) \times 10^{16} \text{ cm}^{-3}$ ]. The authors remark that the maximum of the luminosity is reached later than interference observations indicate that maximum ionization is reached.<sup>71</sup>

A paper by Petschek and others<sup>154</sup> suggested that the distribution of the electron concentration behind the front of a shock wave could be studied by measuring the shift and broadening of lines caused by the Stark effect, using photographs of particular parts of the spectrum on a moving film. Alyamovskii and Kitaeva<sup>1</sup> have developed this method; in their work the image of the spectrum was made to move across a stationary film by placing a rotating slotted disk in front of the slit of the spectrograph. By using the statistical theory of Holtzmark the authors determined from the measured shift and shape of the hydrogen  $H_\beta$  line the concentration of electrons behind a reflected shock wave in argon containing 2 percent hydrogen. Good agreement was found between the measured values of  $N_e$  and the values calculated from the Saha equation for the conditions behind the reflected wave [ $T = 12200 - 13300^\circ \text{K}$ ,  $N_e \sim (1.3 - 1.7) \times 10^{17} \text{ cm}^{-3}$ ]. Unfortunately the resolving time of the sweep mechanism was too large for any conclusions to be drawn about the development of the ionization process. In another experiment<sup>102</sup> to get better resolution in time the image of one of the lines of the spectrum was divided into seven sections; the radiation from each section fell on a photomultiplier. This method was used to study the behavior of the shapes of a number of lines in shock waves in helium and deuterium.

In another method for measuring the electron concentration (already mentioned in a review, reference 56, page 526) one measures the displacement of magnetic lines of force when a volume of the gas ionized by a shock wave comes into a specially designed external magnetic field.<sup>134,135</sup> Special methods of calibration and computation of the emf induced in a measuring coil owing to the displacement of the lines have made it possible to measure the electric conductivity

of argon<sup>135</sup> and air<sup>134</sup> behind the fronts of shock waves. In these experiments also the resolving time is long (about 5  $\mu$ sec); therefore the authors establish only the fact that in air the time for establishing the equilibrium ionization is smaller than the resolving time of the apparatus.

The use of microwaves has great promise for the measurement of small electron concentrations behind shock fronts. One of the first successful researches in this direction used measurements of the distribution of the absorption of radio waves  $\lambda = 3$  cm in shock waves propagated in air (Mach number 8.2 – 10.4) and nitrogen to which 0.25 percent oxygen had been added (Mach number 7.4 – 8.8).<sup>139</sup> The arrangement for measuring the absorption coefficient of the microwaves is analogous to that for optical measurements; on one side of the measuring section of the shock tube there was a 3-cm wave generator, on the other the detector, from which the signal goes to an oscilloscope. The microwaves were sent into the shock tube through an aperture of size  $25.4 \times 12.7$  mm; the axis of the waveguide was perpendicular to the axis of the shock tube. The attenuation of the signal was calibrated by replacing the shock tube by a discharge tube of the same diameter and measuring the concentration of electrons under static conditions (discharge in hydrogen). The authors found that in the range of comparatively weak shock waves investigated the absorption coefficient  $\alpha$  can be written in the form

$$\alpha = \frac{16\sqrt{\pi} e^2 N_e Z}{3 m \omega^2}, \quad (5.9)$$

where  $e$ ,  $m$  are the charge and mass of the electron,  $\omega$  is the angular frequency of the microwaves used, and  $Z$  is the mean collision frequency. In the range of values of  $N_e$  that was studied ( $10^{10} - 10^{12}$  cm<sup>-3</sup>) there is good agreement of the maximum measured values of  $N_e$  with the calculated values; the contribution of impurities to the measured ionization is negligibly small. The authors measured the time necessary for the establishing of the equilibrium ionization (7 – 12  $\mu$ sec) and thus supplemented the results of reference 147 (Fig. 7). It must be noted that the time resolving power was not high; this makes us regard the results as not entirely reliable.

An analogous method has been developed by Bazhenova and Lobastov.<sup>3</sup> Brandt and Kurtmulaev have attempted measurements of electron concentrations in shock waves by an application of a resonator method, which involves essentially observation of the change of the quality figure of a resonator when gas ionized by a shock wave enters its central part. The method of measurement used by these authors is described in reference 7.

**5.6. Measurement of the Pressure.** One of the most convenient indicators of pressure changes in such rapidly occurring processes as the propagation of a shock wave in a gas is a piezoelectric transducer with

a sensitive element of barium titanate. The constructor of such a sensing element is described by Zaitsev.<sup>13</sup> After the action of the shock wave on the barium titanate ceramic an elastic deformation wave is propagated through the ceramic; to prevent the disturbing effect of a reflected wave the ceramic is in acoustical contact with a sufficiently long zinc rod (the acoustic impedances of the ceramic and the zinc are equal). Studies of the pressure distribution made with such sensing elements have shown that within the limits of the "plug" the pressure behind the front of a shock wave in a shock tube remains practically constant, to an accuracy of 2 – 3 percent, and agrees with the calculated value obtained from the conservation laws. The time resolution is determined by the diameter of the ceramic used (5 – 10 mm).

**5.7. Measurement of the Speed of Flow.** In a number of investigations of physico-chemical transformations studies have been made of the effect of nonequilibrium processes on gas-dynamical characteristics: the speed of flow<sup>108</sup> or the speed of a reflected shock wave.<sup>2,175</sup> In these researches Toeppler apparatus was used for photographing (with photo-sweep and flash exposure) the pattern of the gas flow in a shock tube—cf. the review article of reference 56. In this way Feldman<sup>108</sup> has obtained some data on the upper limit on the values of the rate of recombination processes in air; Strehlow and Cohen<sup>175</sup> found that the values they measured (from the speed of a reflected shock wave) for the vibrational relaxation times of O<sub>2</sub> and N<sub>2</sub> agreed with the results of Blackman.<sup>77</sup> Bazhenova and Zaitsev<sup>2</sup> have studied the effect of deviations from equilibrium on the speed of a reflected shock wave in CO<sub>2</sub>. By a similar method Semenov<sup>53</sup> has measured the angle of the oblique secondary shock wave at a wedge inserted in a shock tube, and obtained an estimate of the dissociation energy of nitrogen.

A virtue of these papers is the intuitive character of the results obtained, but to get quantitative results one must overcome great difficulties; these methods do not as yet have good enough resolving power in time.

\* \* \*

Summarizing our survey of the methods of experimental study of relaxation phenomena at high temperatures, we must note that the most productive and promising of these methods are the interferometric method for measuring the density distribution and the spectral methods (using absorption spectra in studying dissociation and the excitation of molecular vibrations, and emission spectra to study ionization and the excitation of electronic levels). This is due both to the strong dependence of the density and spectral characteristics on the state of the gas and to the adaptability and sensitivity of these kinds of apparatus, and also to the possibility of getting sufficiently high resolving

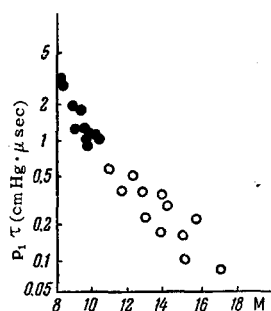


FIG. 7. Time for establishing ionization equilibrium ( $\tau$ ) in air, multiplied by the value of the pressure before the front ( $p_1$ ), as a function of the Mach number for the shock wave (solid circles are data of Manheimer and Low,<sup>139</sup> open circles, data of Niblett and Blackman<sup>147</sup>).

power with respect to time. The experiments have shown that the dimensions of the nonequilibrium zones in which excitation of vibrations occurs behind a shock front remain constant as the wave moves with constant speed along the tube, and do not depend on the geometry of the tube. For example, the sizes of the zone of vibrational relaxation in  $N_2$ , as obtained with various tubes by Blackman<sup>77</sup> and by Bayron,<sup>76</sup> agree to within experimental error; the zones in  $O_2$  are the same in measurements by Generalov and one of the present writers<sup>9,31</sup> and by Blackman,<sup>77</sup> and so on. As for the processes of excitation of electronic levels and of ionization, according to Gloersen<sup>113a</sup> photoelectric emission from the walls of the shock tube may play an appreciable part in the development of these processes in monatomic gases.

## 6. SUMMARY OF RESULTS

In conclusion we shall summarize the results of experimental studies of the nonequilibrium phenomena that accompany the propagation of shock waves. In doing so we shall concern ourselves only with those results that on one hand are definitely reliable, and on the other are most convenient for comparison with theoretical calculations.

6.1. The Establishing of the Maxwell Distribution (Monatomic Gas). Experimental values of the thicknesses of shock waves in argon and helium, as functions of the number  $M$  for the wave, are given in Table III (the mean free path under normal conditions is  $6.9 \times 10^{-6}$  cm in argon and  $1.8 \times 10^{-6}$  cm in helium). It can be seen from this table that the process of establishing the Maxwell distribution occurs in a time which corresponds to several mean free paths. This result is in good agreement with the general conclusions from kinetic theory. The results of a concrete calculation of the thickness of a shock wave in argon are shown together with the experimental data in Fig. 8. The diagram shows that the thickness of the shock wave calculated by Muckenfuss by means of the binomial distribution<sup>119</sup> agrees with experiment. As was to be expected (see Sec. 3.1), the hydrodynamical method of calculation leads to poorer agreement with experiment, and the discrepancy increases with increasing Mach number.

Table III. Values of shock front thickness in monatomic gases

Gas	Speed of shock wave, (Mach number)	Thickness of front (in mean free paths)	Authors	Notation in Fig. 8
Ar	1.23	12.5	Anderson and Hornig <sup>69</sup>	1
	1.37	7.9		
	1.55	6.1		
	1.34	10.1	Talbot and Sherman <sup>178</sup>	3
	1.46	8.1		
	1.58	6.6		
	1.73	5.5		
	1.26	12.1		
	1.33	10.0	Hansen and Hornig <sup>119</sup>	2
	1.51	7.3		
	2.38	4.3		
	3.0	4.4	Ballard and Venable <sup>74</sup>	4
	4.0	3.0		
	5.8	8.5		
	1.6	>6.5	Duff and Webster <sup>106</sup>	5
3	6.5			
7	>6.5			
He	1.73	4.7	Sherman <sup>171</sup>	—
	1.83	4.5		

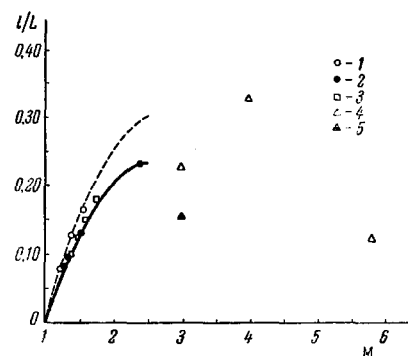


FIG. 8. Ratio of the mean free path  $l$  to the shock front thickness  $L$ , as a function of the Mach number of the shock wave. The solid line is calculated by means of the binomial distribution,<sup>119</sup> and the dashed line is calculated from the Navier-Stokes equations. For the notations 1-5, see Table III.

We note that, in agreement with the results of studies with an electron beam,<sup>74,105</sup> the thickness of the wave has a minimum near Mach number 3-4. This fact has not yet received an explanation.

6.2. Rotational Relaxation. The experimentally measured values of the number of collisions  $Z_{rot}$  necessary for the establishing of rotational equilibrium in chlorine, nitrogen, and oxygen are shown in Table IV. For this purpose  $Z_{rot}$  is defined as the ratio of  $\tau_{rot}$ , the time for the establishing of rotational equilibrium, to  $\tau_{col} (2\nu\sigma^2)^{-1} (m/2\pi kT)^{1/2}$ , the mean time between collisions. For greater completeness Table IV includes data from ultrasonic measurements (cited in reference 149). For comparison we also give in the table the theoretically calculated results obtained in reference 149.

As can be seen from Table IV, the process of rotational relaxation of heavy molecules occurs in a time corresponding to several free paths. In this case

Table IV. Number of collisions  $Z_{rot}$  necessary for the establishing of equilibrium in the rotational degrees of freedom of molecules ( $T = 300^\circ\text{K}$ )

Gas	$Z_{rot}$		Method of determination	Authors
	theory	experiment		
Cl <sub>2</sub> N <sub>2</sub>	4.90	5.5	Shock wave	Anderson and Hornig <sup>70</sup>
	4.01	6	Ultrasonic	Zmuda <sup>191</sup>
O <sub>2</sub>	3.45	3	"	Parker et al. <sup>150</sup>
		5	"	Tempest and Parbrook <sup>179</sup>
		5.26	"	Greenspan <sup>116</sup>
		5.5	Shock wave	Anderson and Hornig <sup>70</sup>
		3	Ultrasonic	Parker et al. <sup>150</sup>
		12	"	Connor <sup>100</sup>
		5	"	Tempest and Parbrook <sup>179</sup>
		5	Shock wave	Anderson and Hornig <sup>70</sup>

the time for establishing rotational equilibrium is practically the same as that for establishing the Maxwell distribution. In a shock wave the processes of establishing the Maxwell distribution and rotational equilibrium occur in parallel, and in the case of sufficiently heavy gases can scarcely be distinguished. An

approximate theoretical calculation of the number of collisions  $Z_{rot}$ , based on the classical picture of the interaction of two rotators, leads, as we see from the table, to satisfactory agreement with the experimental data. It must be emphasized, however, that the theoretical calculation carried out in Sec. 3.3 is of a qualitative nature. Exact calculations for this case are difficult because the processes of establishing the Maxwellian and rotational equilibria overlap.

6.3. Vibrational Relaxation. Table V shows experimental values of the rotational relaxation time of the diatomic molecules O<sub>2</sub>, N<sub>2</sub>, Cl<sub>2</sub>, CO, NO; as in the preceding section, these data are supplemented by some results of acoustical measurements. Table VI shows values of the relaxation time in CO<sub>2</sub> and N<sub>2</sub>O, obtained by the use of shock tubes.

Figure 9 shows the dependence of the number of collisions  $Z_{vib}$  necessary of the establishing of vibrational equilibrium on the adiabatic factor  $\omega\tau^*$ . Here we have taken  $Z_{vib} = \tau_{vib}/\tau_{col}$ , where  $\tau_{vib}$  is the measured relaxation time and  $\tau_{col}$  is the time between collisions. The value of the adiabatic parameter  $\omega\tau^*$  has been calculated from the relation

Table V. Values of the vibrational relaxation time in pure diatomic gases

Gas	Temperature range, °K	Range of measured values of $\tau_{vib}$ ( $\mu\text{sec}$ ) at $p = 1\text{ atm}$	Method of determination	Authors
O <sub>2</sub>	292	3180	Acoustical (Kundt tube)	H. Knötzel and L. Knötzel <sup>133</sup>
	300	1000	Acoustical (reverberation method)	Kneser and Knudsen <sup>130</sup>
N <sub>2</sub>	770-3150	60-1.2	Shock wave (interferometer)	Blackman <sup>77</sup>
	2450-10000	5.0-0.17	Shock wave (absorption spectroscopy)	Generalov and Losev <sup>9,31</sup>
	778-1186	1760-796	Acoustical	Lukasik and Young <sup>136</sup>
	1470	230	Shock wave (interferometer)	Blackman <sup>78</sup>
	3000-4400	38.3-6.5	" "	Bayron <sup>76</sup>
Cl <sub>2</sub>	3500-5600	19.0-4.7	" "	Blackman <sup>77</sup>
	241-415	6.3-1.6	Acoustical	Eucken and Becker <sup>107</sup>
	248-273	7.5-4.7	"	Schulze <sup>168</sup>
CO	575-1470	1.5-0.4	Shock wave (interferometer)	Smiley and Winkler <sup>174</sup>
	1273-2073	10	Acoustical	Sherrat and Griffith <sup>172</sup>
	1470	19	Shock wave (infrared spectroscopy)	Windsor, Davidson, and Taylor <sup>190</sup>
	2200-3500	10-2.7	Shock wave (interferometer)	Greenspan and Blackman <sup>115</sup>
NO	2000-5000	50-2.2	" "	Matthews <sup>144</sup>
	450-1300	0.47-0.17	Shock wave (absorption spectroscopy)	Robben <sup>161</sup>

Table VI. Values of the vibrational relaxation time for triatomic gases, obtained by the use of shock tubes

Gas	Temperature range (°K)	Range of measured values of $\tau_{vib}$ ( $\mu\text{sec}$ ), for $p = 1\text{ atm}$	Possible type of vibrations and corresponding characteristic temperature $\theta$	Authors
CO <sub>2</sub>	300-1250	5.2-0.85	Deformational vibrations, $\theta = 959^\circ\text{K}$	Griffith, Brickl, and Blackman <sup>117</sup>
	360-600	2.32-0.76	$\theta = 959^\circ\text{K}$	Resler and Scheibe <sup>158</sup>
	380-1000	5.0-0.4	$\theta = 959^\circ\text{K}$	Smiley and Winkler <sup>174</sup>
	600	2	$\theta = 959^\circ\text{K}$	Greenspan and Blackman <sup>115</sup>
	2200	3.5	Symmetrical valence vibrations, $\theta = 1920^\circ\text{K}$	Greenspan and Blackman <sup>115</sup>
N <sub>2</sub> O	2520-2720	54-6	Not determined	Hurle and Gaydon <sup>126</sup>
	305-840	1.4-0.3	Deformational vibrations, $\theta = 847^\circ\text{K}$	Griffith, Brickl, and Blackman <sup>117</sup>

$$\omega\tau^* = \frac{2\pi\Delta E}{v^*\alpha^*h},$$

where  $\Delta E$  is the size of the first vibrational quantum,  $v^*$  is the relative velocity of molecules for which collisions are important in the excitation of vibrations [in accordance with reference 169 it has been assumed that  $v^* = (4\pi^2kT\Delta E/\alpha^*h\mu)^{1/3}$ ], and  $\alpha$  is the reciprocal of the radius of intermolecular interaction [for an interaction potential taken in the form  $V = V_0 \exp(-\alpha r)$ ]. The quantity  $\alpha$  was determined by comparison with the Lennard-Jones potential by the two-point method described by Herzfeld and Litovits,<sup>123</sup> the parameters  $r_0$ ,  $\epsilon$  of the Lennard-Jones potential were taken from reference 124 and correspond to the temperature range 300 – 1000°K studied earlier. An iteration method was used to determine the value  $\alpha^* = \alpha(v^*)$ ; in practice it turned out that  $\alpha$  and  $\alpha^*$  are nearly equal. On the other hand it was found that  $v^*$  is always several times the mean thermal velocity  $\bar{v}$  of the molecules at the given temperature.\*

It can be seen from Fig. 9 that for the majority of the gases the experimental points  $Z_{\text{vib}} = Z_{\text{vib}}(\omega\tau^*)$  lie on one curve. This means first of all that the mechanisms of excitations of the vibrations in these gases are of the same nature. A comparison of the theoretical calculations with the experimental data

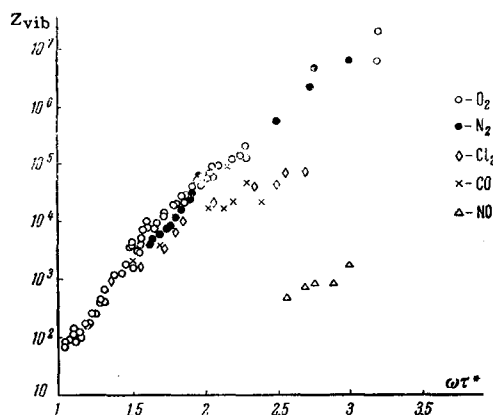


FIG. 9. Dependence of the number of collisions  $Z_{\text{vib}}$  necessary for the establishing of vibrational equilibrium in a diatomic gas on the adiabatic factor  $\omega\tau^*$ .

for oxygen, which has been made in Sec. 3.2 over a wide range of temperatures, shows that the assumption of the adiabatic mechanism of the excitation of vibrations is correct. Thus we can assert that for the majority of the molecules considered here the mechanism of excitation of vibrations in molecular collisions is an adiabatic one. As can be seen from Fig. 9, NO is an exception to this rule. An interesting attempt to interpret this result by treating the excitations as nonadiabatic has been made in reference 44.

\*Kneser<sup>131</sup> gives the dependence of  $Z_{\text{vib}}$  on  $\omega\tau$ , where  $\tau$  is the time of contact of the molecules in a collision, calculated as a function of  $v$ . Since the important velocity in the excitation of molecular vibrations is  $v^*$ , the interesting relation is that giving the dependence of  $Z_{\text{vib}}$  on  $\omega\tau^*$  as a function of  $v^*$ .

For larger values of  $\omega\tau^*$  there is also a small spread for other molecules. Since, however, for smaller values of  $\omega\tau^*$  the data for  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{Cl}_2$ , and  $\text{CO}$  lie on a single curve, there is scarcely a basis for asserting that the process of excitation of vibrations in these molecules is not adiabatic.

In Fig. 10 these same results are represented in terms of the dependence of  $P_{10}$  on the value of  $T^{-1/3}$ . Here, as usual, it is assumed that  $P_{10} = \{\tau_{\text{vib}} Z \times [1 - \exp(-\Delta E/kT)]\}^{-1}$ . This diagram is convenient for comparison of the experimental data with the theory of Landau and Teller. According to this theory the relation between  $\ln P_{10}$  and  $T^{-1/3}$  is linear (cf. Sec. 2). It can be seen from Fig. 10 that a linear relation between  $\ln P_{10}$  and  $T^{-1/3}$  holds only over small temperature intervals. The experimental points cannot be approximated by a single straight line over the entire range of temperatures. One cause of this is evidently that the radius  $\alpha^{-1}$  of the intermolecular forces does not remain constant. On the other hand, by comparing the theoretical and experimental values we can determine the value of  $\alpha$ , i.e., the potential of the intermolecular interaction, over each small temperature interval. This is especially important for temperatures of the order of several thousand degrees, where older methods for determining the potential of the intermolecular interaction are not valid.

6.4. Dissociation of Diatomic Molecules. Experimental values obtained by means of shock tubes for the rate constant of thermal dissociation of diatomic molecules are shown in Table VII. Values of the coefficient  $P$  of the exponential in the Arrhenius expression for the rate constant,  $k = PZ \exp(-D/kT)$ , are shown in Fig. 11, plotted against the values of  $(D/kT)^{3/2}$ .

It can be seen from Fig. 11 that the experimental values of the coefficient  $P$  form two groups. The first group corresponds to dissociation rate constants that describe dissociation in homogeneous systems, that is, dissociation in an atmosphere of the gas itself. The second group corresponds to dissociation rate con-

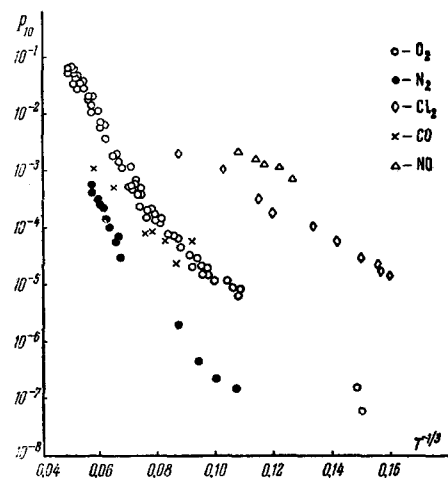


FIG. 10. Probability  $P_{10}$  for deactivation of the first vibrational level.

Table VII. Values of the rate constant for thermal dissociation of diatomic molecules, obtained by means of shock tubes

Dis-sociating gas	Diluting gas	Temperature range, degrees	Range of values obtained for $K$ ( $\text{cm}^3 \text{mole}^{-1} \text{sec}^{-1}$ )	Method of determination	Authors	Notation in Fig. 11
O <sub>2</sub>	O <sub>2</sub>	2400—4500	$1 \cdot 10^8$ — $1.5 \cdot 10^{10}$	Interferometer	Matthews <sup>143</sup>	Solid line 2
		2580—4000	$1 \cdot 10^8$ — $2.7 \cdot 10^9$	"	Bayron <sup>76</sup>	Solid line 3
		3000—3500	$2.7 \cdot 10^8$ — $1.6 \cdot 10^9$	Absorption spectrum	Losev <sup>26</sup>	Solid line 1
O <sub>2</sub>	(25% Xe)	3400—3500	$1.4 \cdot 10^8$ — $4.1 \cdot 10^8$	Absorption of x-rays	Chesik and Kistiakowsky <sup>93</sup>	○
O <sub>2</sub>	Ar	3300—5680	$2.5 \cdot 10^7$ — $3.1 \cdot 10^{10}$	Absorption spectrum	Camac et al. <sup>86</sup>	×
Br <sub>2</sub>	Br <sub>2</sub>	1010—1610	$1.7 \cdot 10^7$ — $1.3 \cdot 10^9$	"	Palmer and Hornig <sup>146</sup>	Upper dashed line
Br <sub>2</sub>	Ar	1310—2225	$8.9 \cdot 10^7$ — $1.2 \cdot 10^{10}$	"	"	Lower dashed line
		1400—1800	$8.7 \cdot 10^7$ — $2.7 \cdot 10^9$	"	Britton et al. <sup>84</sup>	Lower dashed line
I <sub>2</sub>	Ar	1040—1630	$5.6 \cdot 10^7$ — $9.5 \cdot 10^9$	"	Britton et al. <sup>82</sup>	Lower solid line
I <sub>2</sub>	N <sub>2</sub> (unexcited)	1000—1560	$2.2 \cdot 10^7$ — $1.5 \cdot 10^{10}$	"	"	Dash-dot line
		CO <sub>2</sub>	1120	$1.65 \cdot 10^8$	"	Britton et al. <sup>83</sup>
I <sub>2</sub>	O <sub>2</sub>	1275	$8.8 \cdot 10^8$	"	"	□
	He	1400	$1.01 \cdot 10^9$	"	"	★

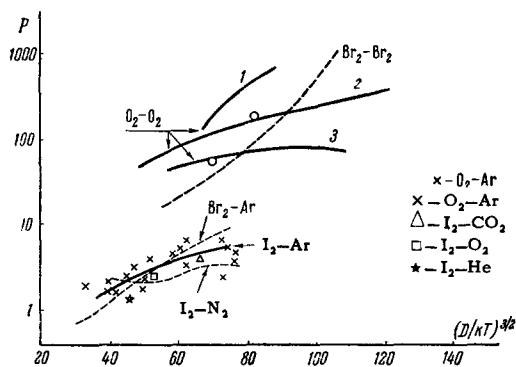


FIG. 11. Coefficient  $P$  of the exponential in the expression for the rate constant for thermal dissociation, for iodine, bromine, and oxygen. For notations see Table VII.

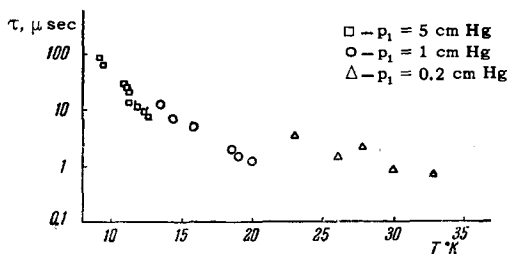


FIG. 12. Time  $\tau$  for the establishing of the equilibrium ionization in argon, as a function of the atomic temperature. The abscissa is  $T_A$  in units  $10^3$  °K.

stants for dissociation in atmospheres of monatomic gases or certain other gases. For these two groups the coefficients of the exponential differ by about an order of magnitude. This means that the rate of dissociation in a homogeneous system is an order of

magnitude larger than that in the medium of a monatomic gas.

The difference in the dissociation rates is most likely due to participation of the internal degrees of freedom of the incident particle in the process of dissociation.

It can also be seen from Fig. 11 that the theoretical relation  $P = P [(D/kT)^{3/2}]$  does not always give a good representation of the connection between  $P$  and  $T$ .

6.5. Ionization. As has already been indicated, the number of experimental papers devoted to the determination of the time for the establishing of the equilibrium ionization is very small, and the results are not always reliable. Owing to this we confine ourselves to the data of Petschek and Bayron,<sup>153</sup> which were obtained for the case of the ionization of argon. Figure 12 shows values of the time  $\tau$  for the establishing of the equilibrium ionization, as obtained in reference 153, plotted against the atomic temperature  $T_A$ , which is established immediately behind the shock front and before the beginning of the ionization process (only the data for argon of the highest purity attained are used). From Fig. 12 we can only draw conclusions regarding the order of magnitude of the time  $\tau$  for the establishing of the equilibrium ionization and about the amount of change of  $\tau$  with temperature. In spite of the great practical importance of the ionization process, the kinetics of this process is in many respects not yet clear.

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Translated by W. H. Furry